

Hyper baric carburising process

E. Gianotti

A new patented technology improves low pressure carburising in vacuum furnace and traditional carburising in sealed quench furnace.

The author, starting from argument that is possible to see in the specialized publications on the subject, has examined by scientific criteria which are the limits and the advantages of both the low pressure carburising ,or the controlled atmosphere process. He evaluates the technological possibility to overcome some of the limits that are conditioning the mechanical property of the heat treated pieces. Before suggesting new technological solutions that can promote better metallurgical properties together with clean environment, he examine some scientific arguments to make clear the problems.

At the end of this research some important technological modification will be realised and the obtained results confirm the validity of the new process of hyper baric carburisation.

The cause of the defects arising from the traditional technology have been eliminated and the modifications requested on the furnaces are not expensive. In some cases, maybe the new furnaces are even cheaper, both in the buying phase than in the running cost.

Key words: steel, carburising, heat treatment, plants and fixture

INTRODUCTION

The low pressure carburising has already reached a good diffusion in the heat treatment market .

Compared with the old traditional controlled carburising atmosphere, it has the big advantages of being near pollution free.

Some other advantages claimed by vacuum furnace builders have some difficulty being demonstrated by practical application, as it's possible to see in the specialized publications on the subject.

Avoiding taking into consideration some less technical arguments like cost effectiveness, speed of carbon penetration, and furnace and facility cost , the most stimulating discussions are about the technological property of the product, compared with the others obtained with the old controlled atmosphere.

The most discussed arguments are the fatigue strength and the toughness that are conditioned by:

- Surface decreasing of alloying elements.
- Inter granular oxidation.
- Speed of cooling in the quench step, using gas or gas mixture up to 20 bars.

You can read about this subject in the bibliography at the end of this work 1) , 2) , 3).

Starting from this argument, the author has examined, by scientific criteria, which are the limits and the advantages of both the low pressure carburising ,or the controlled atmosphere process. He evaluates the technological possibility to overcome some of the limits that are conditioning the mechanical property of the heat treated pieces.

Before suggesting new technological solutions that can promote better metallurgical properties together with clean environment, we need to examine some scientific arguments to make clear the problems.

- a) Solid-gas phases equilibrium of the metals to high temperature.
- b) Thermodynamic equilibrium of the surface inter granular oxidation that can happen during the carburisation with

endogas or in the vacuum furnace if there are too many vacuum leaks.

- c) The quenching in gas, when the heat treatment is made in vacuum furnace, is too slow, also if it's made with high pressure or blending of same expensive gas like He. In this case the toughness is lower than the quenching in oil. (See the bibliography 3) by Fernando Da Costan just quoted).

SOLID-GAS PHASES EQUILIBRIUM OF THE METALS IN FURNACE TO HIGH TEMPERATURE

Metals evaporation in vacuum furnace

Every metal has a tension, or pressure of evaporation, that is only temperature dependent (see tab 1.)

In an imaginary vacuum furnace, without leakage, if the absolute pressure that can reach the vacuum pump is lower than the evaporation tension of the metal, the metal evaporates continuously and goes to solidify on the cold walls of the furnace or of the pump that have a temperature lower than the metal evaporation. The remaining part of the vapour is eliminated by the pump.

The metal that solidifies on cold walls decreases the partial pressure in the furnace, so other metal can evaporate.

In the event where the absolute pressure generated by the pump is not lower than the metal evaporation tension, the metal vapour , also if it has saturated the furnace chamber , cannot be extracted by the vacuum pump. It can also, in this event, solidify on the cold walls if these are at the temperature lower than the solid-gas equilibrium and allows further evaporation of the metal surface.

In the more realistic event in which the furnace has some leakage, and if the vacuum pump is not able to reach value lower than metal evaporation pressure, some metal vapour can be sucked together with the air from the leakage, breaking the equilibrium of the 'solid metal - vapour ' and permitting again the evaporation of the metal surface.

Therefore, in every event, the heating of the steel in the vacuum furnace generates a continuous loss of alloying elements from the surface. Only in the purely theoretical event of a vacuum furnace without leakage, with the inner walls at the same working temperature of the furnace and the vacuum pump isolated, would it be possible to avoid continuous evaporation of the alloying elements.

Elio Gianotti
Trattamenti Termici Ferioli & Gianotti SpA - Rivoli Torino Italy

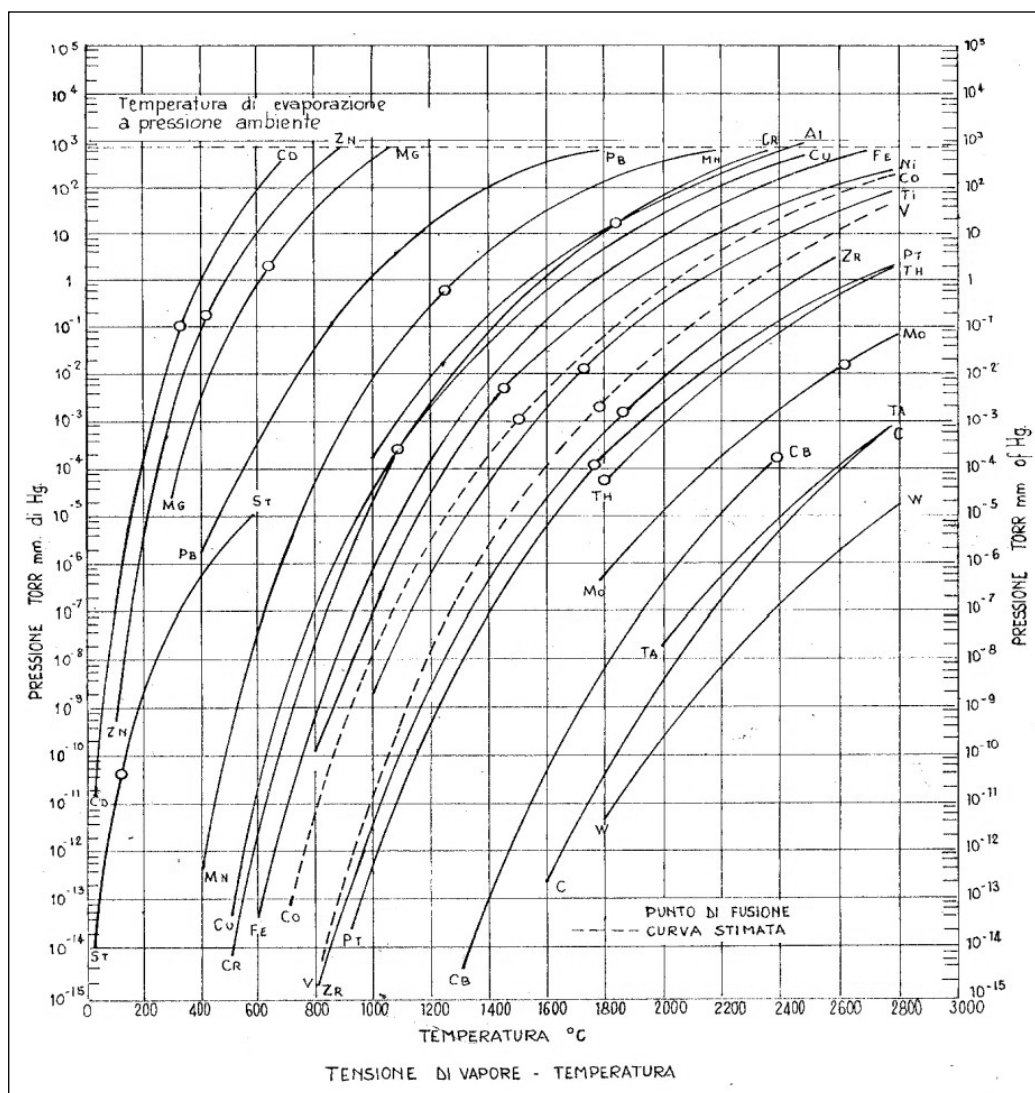


Table 1 – Vapour tension of metals in the range 0° to 2800°C.

Tabella 1 – Tensione di vapore dei metalli a temperature da 0 a 2800°C.

Metals evaporation in controlled atmosphere furnace

Also in this furnace, the metal's vapour tension generates an impoverishment on the steel's surface that is more important as the temperature goes higher. The impoverishment will be higher in the alloying metals that have a higher tension (see table 1), so the surface composition can vary in its alloying elements.

The impoverishment in this event is linked to the passage of carburising gas over the pieces' surface.

It's not easy to say which of the two furnaces is more reliable regarding this problem, because many variables are to be considered.

The vacuum furnace, with a good seal, surely has a lower number of atmosphere changes compared with the atmosphere competitor, but it has a great surface of cold walls that makes easy the vapour deposition of the alloying metals and can generate other evaporation.

To avoid evaporation loss of alloying metals, considering that it is not possible to change the evaporation equilibrium, it's only possible to decrease the atmosphere change in the furnaces and to maintain the walls' temperatures near the process temperature.

Utilizing low pressure carburisation by a vacuum furnace, the process temperature can arrive up to 1.000° C . At this temperature the Mn is the metal that has the highest vapour tension, followed in decreasing order by Al, Cu, Cr. It may be considered that the Mn vapour tension at 1.000°C is about 10⁻² mbar, while the absolute pressure at the furnace during the carburising process is about 10-30 mbar, so the vacuum is not too dangerous.

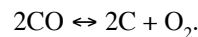
To better value the dangerous effect of the evaporation of alloying elements in vacuum furnace and particularly in the low pressure carburising process, see in the bibliography the work of B.Clausen 1) and Y. Bienvenu, K Vieilleveigne 2).

THERMODYNAMIC EQUILIBRIUM OF INTER GRANULAR OXIDATION

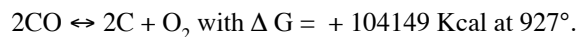
Carburising process in controlled atmosphere

The most utilized atmospheres are the endogas and the nitrogen-methanol . In both cases the blend of the gas is formed by about 20% of CO that is the most important in the exchange of the C from the atmosphere to the surface of the carburising steel.

The schematic reaction is the following:



The free energy ΔG of the reaction at 927° C (1200 K) calculated by the Barin Knacke parameter is



The constant K of the reaction will be:

$$\ln K = - 104.149 / (1,987 \cdot 1200) = - 43,68 \text{ so } K = e^{-43,68}$$

but $K = p(O_2) / p(CO_2)^2$ than substituting the values will be:

$$p(O_2) = e^{-43,68} \cdot 0,2^2 = 4,3 \cdot 10^{-21} = 10^{-20,37}$$

This value of p(O₂) generates about 1.140 mVolt in the oxygen probe (see Nerst formula) and is equivalent to a car-

bon potential of about 0,80% (see oxygen probes tables). It is so demonstrated that in the carburising atmosphere there is a pO_2 equal to near 10^{-20} and thereafter every element that is in such atmosphere, with a chemical equilibrium with the oxygen partial pressure equal or lower, will become an oxide.

In table 2 there are some alloying elements that are always in the steel, also like impurity, with the relative partial oxygen pressure in equilibrium at $900^\circ C$ with the element in the oxidising chemical reaction.

Note as the metals Cr, Mn, Si, Al, normally present in the inter granular oxidation, oxidise with pO_2 from 10^{-24} to 10^{-36} . To avoid their oxidation, it is necessary to operate with pO_2 below 10^{-36} .

For more detailed information about the inter granular oxidation in the atmosphere controlled furnace, see ref.4).

Low pressure carburising process in vacuum furnace

Both in the low pressure carburising process or in plasma carburising process (ionic discharge), the working pressure in the furnaces are about 10 – 200 mbar.

Also, when the process is starting and there is the need to clean the chamber and the pieces, the higher vacuum reached by the pump is $10^{-4} - 10^{-5}$ bar; that is a vacuum very far from the $10^{-36}/0.21$ bar necessary to avoid the inter crystalline oxidation.

The purity of the furnace is not sufficient, but the continuous introduction of high purity carburising gas, as N_2 , Ar_2 or hydrocarbon like C_3H_8 , CH_4 , C_2H_2 or other, washes the atmosphere until it arrives at the needed purity.

Normally, with furnaces with good sealing, it is possible to arrive at the end of the process, avoiding inter granular oxidation.

The furnace sealing may deteriorate if the maintenance is not good. In this event, if the furnace absorbs air from the leakages, the oxygen concentration may increase over 10^{-36} , and the inter crystalline oxidation occurs.

STIRRING OF CARBURISING ATMOSPHERE

While in the controlled atmosphere furnace it is possible to homogenize easily the atmosphere composition in the inner furnace by one or more fans, it is more difficult to avoid stratifications or non uniformity in the vacuum furnace. There are some systems realized, the most curious has been made up by an important furnace builder in U.S. He has mounted a big fan in the furnace chamber.

The non uniformity in the atmosphere may generate hardness and case depth problems.

Réactions	$P(O_2)$ [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

Table 2 – Partial pressure $p(O_2)$ in equilibrium at $900^\circ C$ with the metals oxide and the CO and H_2 .
Data obtained from Ellingham-Richardson diagram.

Tabella 2 – Equilibrio a $900^\circ C$ della $p(O_2)$ con gli ossidi dei metalli elencati e con l'idrogeno e il CO.
Valori ricavati dal diagramma di Ellingham-Richardson.

THE NEW HYPER BARIC TECHNOLOGY ELABORATION

After we have seen all the advantages and the lacks of the old technologies, it is possible to engineer a new technology that takes into account only the advantages and eliminates the defects.

In the low pressure carburisation, the problems are:

- Evaporations of alloying elements determined by low pressure and cold walls
- Few homogeneity of carburisation in the different zone of the furnace.
- Not satisfactory toughness due to slow cooling in the gas quenching.

In the controlled atmosphere carburisation the problems are:

- Environmental, because of the pollution of atmosphere gas and quenching oil
- Inter crystalline oxidation with case depth proportional to square root of time, due to O_2 existing in the endogas.
- Evaporations of alloying elements determined by carburising atmosphere exchange.

Vacuum furnace modifications

It's possible to avoid the a) and b) defects by modifying the furnace so that it can work above the atmospheric pressure.

The cold wall will be thermally insulated using ceramic fibre or other light insulating materials and inner this insulation will be placed a strong, atmosphere tight crucible that also has the task of sustaining the carburising load.

It will be necessary to change the instruments for the vacuum regulation by instruments suitable for regulation of overpressure.

The vacuum pump may be eliminated otherwise, if existing may be utilised to clean more rapidly the furnace atmosphere. After five or more atmosphere changes by cryogenic nitrogen, with purity of 5 ppm O_2 , the furnace will be held in light pressure, normally 500 mm of water. This way, it will avoid air entrance by possible leakage.

The carburising atmosphere must be agitated by a fan to guarantee the carburisation homogeneity.

To avoid the problem c) about the insufficient toughness, the unique solution is the oil quenching, so it is necessary to make provisions for an oil tank below the atmosphere quenching chamber. This is particularly useful for the commercial heat treatments that sometimes have many chemical steel compositions in the same load.

Atmosphere furnace modifications

The furnace must be modified with an addition in the inner part of a strong, atmosphere tight, crucible that has also the task of sustaining the carburising load, both in heating chamber or in the quenching zone. Also, the over pressure security valve must be gas tight.

After this modification, the furnace can work as described in a vacuum modified furnace, with a tight nitrogen atmosphere. This is the condition to avoid the problem scheduled in d) and f), determined by the flow of the endothermic atmosphere.

ELIMINATION OF INTER CRYSTALLINE OXIDATION

Examining tab. 2, it is possible to note that for avoiding the alloying element oxidation, that is the origin of the inter granular oxidation, it is necessary to keep the oxygen partial pressure below 10^{-36} .

With the modification made with respect to the traditional furnaces, both vacuum or traditional controlled atmosphere, it is possible to arrive at a sealed chamber, delimited by a crucible made in refractory steel, with leakage almost inexistent and at worst with the gas that goes out and not with the air that enters to damage the carburising atmosphere.

Fig. 1 – Hyper baric sealed quench furnace featured with the most important modifications compared to vacuum or controlled atmosphere furnace.

- 1) Water cooled sealing gasket in the outer door.
- 2) Over pressure bleeder with sealing, temperature resistant.
- 3) Stirring fan for carburising atmosphere.
- 4) Quenching chamber with oil or pressurized gas.
- 5) Computerized control of nitrogen during the cleaning, the carburising, and the quenching time.
- 6) Inner door.
- 7) Carburising computerized control, according to the boost-diffusion cycle, with hydrocarbon like propane, cyclohexane alcohol.

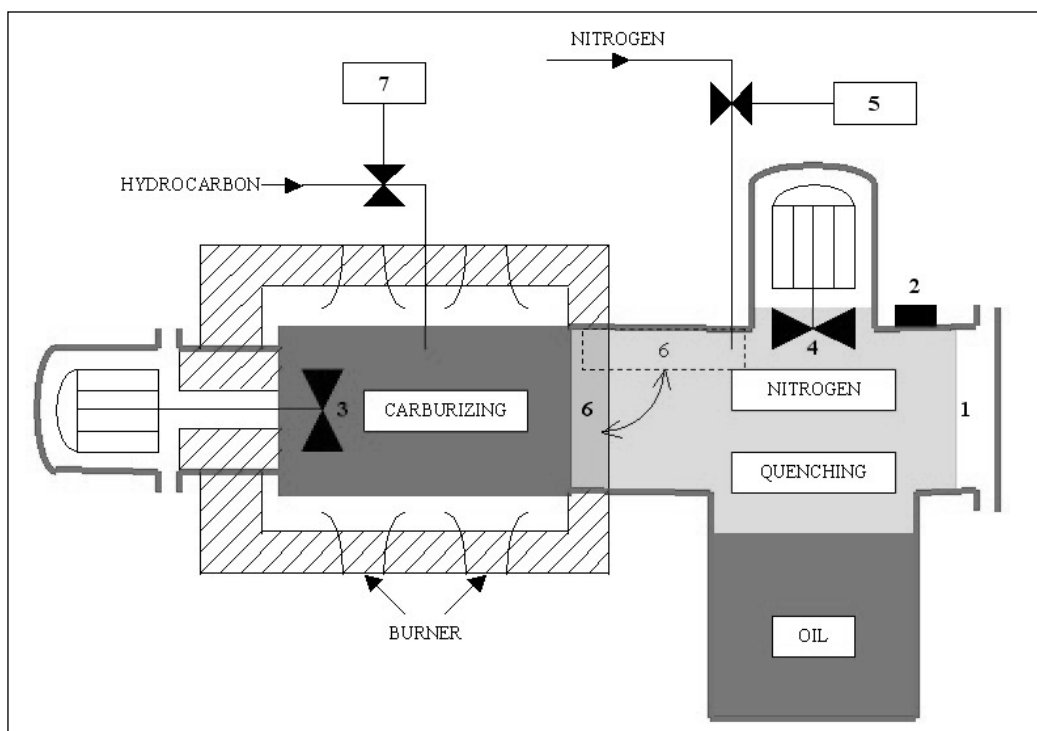


Fig.1 – Impianto a camera per la cementazione iperbarica con evidenziate le principali modifiche rispetto ai forni a vuoto e ad atmosfera controllata.

- 1) Guarnizione di tenuta atmosfera, raffreddata ad acqua, per la porta anteriore
- 2) Sfiatore di sovrappressione, con guarnizione a tenuta termica, per permettere l'uscita di gas caldi o fiamme.
- 3) Ventilatore di omogeneizzazione nella camera di carburazione coibentata.
- 4) Sistema di raffreddamento in azoto nella precamera fredda.
- 5) Sistema computerizzato di controllo e regolazione della pressione dell'azoto durante il lavaggio, la carburazione e l'eventuale tempra in azoto.
- 6) Porta intermedia del forno.
- 7) Sistema computerizzato per la cementazione secondo il ciclo boost-diffusion con idrocarburi (propano, acetilene, alcool cicloesano).

The atmosphere composition in the carburising crucible is cryogenic nitrogen with about 5 ppm O₂ that is O₂ = 5.10⁻⁶. The purity of atmosphere is not sufficient to avoid inter granular oxidation, also in the event of many changes of nitrogen before starting the carburising.

In the furnaces derived from vacuum technology, the cleaning may be accelerated using the vacuum pumps, and without them may be utilized the formula referred to point 5 of bibliography).

The furnace is normally atmosphere tight, and possible leakage doesn't permit air to enter, but only nitrogen to go out from the crucible. In this case some other nitrogen will be introduced to restore the hyper baric pressure.

If the furnace atmosphere purity is the same as the cryogenic nitrogen, that is 5.10⁻⁶, to arrive at the needed value of 10⁻³⁶, it is necessary to eliminate still O₂. For example, an industrial furnace with a crucible volume of about 1 m³, equal to 44,64 gas moles, contains about 44.64·32·5·10⁻⁶ = 0.0071 g of O₂. In the event of oxygen concentration equal to 10⁻³⁶ the O₂ content will be 44.64·32·10⁻³⁶ = 1.428·10⁻³³ g of O₂. So it is necessary to eliminate 7 mg of O₂ from the furnace atmosphere to be sure to avoid the inter granular oxidation.

Only for curiosity, utilising the Avogadro number N_A = 6.02·10²³ mole⁻¹, it's possible to calculate that a concentration of O₂ = 10⁻³⁶ corresponds to about 6.02·10⁻¹³ molecule of O₂ every 22.4 litre of gas, that is one molecule of O₂ every (22.4 / 6.02) 10¹³ litre, or 3.7·10¹⁰ m³ of gas. This value is so little that is impossible to measure it.

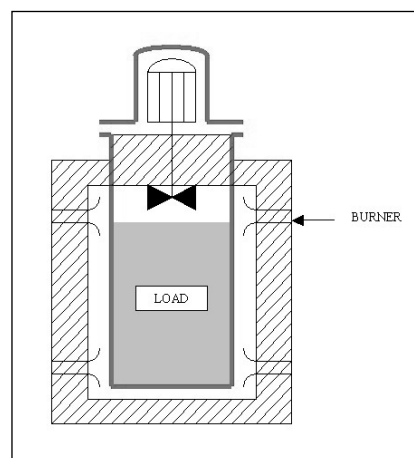
To overtake this problem, there is an innovative idea of the hyper baric carburisation. To put in the atmosphere tight crucible with the load, a thin metal shaving or metal sponge with an equilibrium pressure of oxidation to 1,000°C below 10⁻³⁶ volumes of O₂.

One metal that is easy to find with this characteristic is the

Fig. 2 – Hyper baric pit furnace featured with the most important modifications compared to controlled atmosphere pit furnace.

In this case the quenching is made out of the furnace.

Fig. 2 – Impianto a pozzo per la cementazione iperbarica con evidenziate le più importanti modifiche rispetto al forno a pozzo ad atmosfera controllata. In questo caso la tempra dovrà essere fatta in una vasca esterna al forno.



Titanium (see tab 2).

The shaving or the sponge must be very light, and must be loaded in the furnace with the pieces to be carburised. The free energy (ΔG) of the chemical reaction between Ti and O₂ is lower than that of the alloying element of the steel, so that the most part of atmosphere oxygen is captured by the Ti, and avoids forming inter granular oxidation.

The weight, or better the surface of the Ti sponge or shaving must be sufficient to react with all the oxygen in the atmosphere, therefore it is important, more than the weight, that can be ten - twenty grams, the surface extension of the Titanium. It is best to put it near the fan where there is a good agitation of the atmosphere.

THE HYPER BARIC CARBURISING PROCESS

The carburisation can start when the crucible is full of clean cryogenic nitrogen and in pressure by introducing hydrocarbons, like that utilized in the low pressure process.

The quantity of hydrocarbons, the time of introduction, and the time of diffusion are the same as the boost-diffusion process in vacuum furnace. The technology of carbon enrichment is the same because it is not possible to analyze the atmosphere like in the controlled atmosphere furnace.

It is possible to theoretically foresee the boost and diffusion time utilizing some algorithm obtained from practical experiment (see 'Algorithm for carbon diffusion computation in a vacuum furnace' ref. 6) . Moreover, it is easier than in the vacuum furnace to take out the furnace samples to control the surface carbon content by spectrometer and the case depth.

It is correct to remember that the oxygen probe is not suitable to control the inter crystalline oxidation because it's not sensible enough. The highest signal utilisable with confidence is 1,200 mV. Applying the Nerst formula:

$$mV = 0.0496 \cdot K \cdot [\log O_2(\text{air}) - \log O_2(\text{furnace})].$$

It is possible to calculate the minimum partial pressure of O₂ that can read the oxygen probe for a temperature of 1.200K that is 927°C:

$$mV_{1200} = 0.0496 \cdot 1200 (-0.678 - \log x)$$

calculating $x = -20,84$,
therefore $pO_2 = 10^{-20,84}$.

The oxygen probe may be therefore only utilized like an alarm sensor, to signal some anomalous situation in the atmosphere or in the cleaning of the crucible.

In the fig. 3 there is a picture of the little laboratory furnace utilized for the first carburising tests with cryogenic nitrogen with 5 part for million of O₂, Titanium shaving and propane. The crucible volume is about 1,000 cm³.

Before starting the steel sample to be carburised is loaded in the crucible that is successively sealed. Then the crucible is washed by five change of nitrogen atmosphere. After the last change, the pressure in the crucible was put 500 mm of water column.

At this point can start the heating cycle. When the furnace arrive in temperature the propane can be introduced.

The boost period was 30 minutes and the diffusion time 2 hours. No addition of nitrogen has been necessary during the 2.30 h of the whole cycle.

The temperature was 950°C and the sample 18 Ni Cr Mo 4

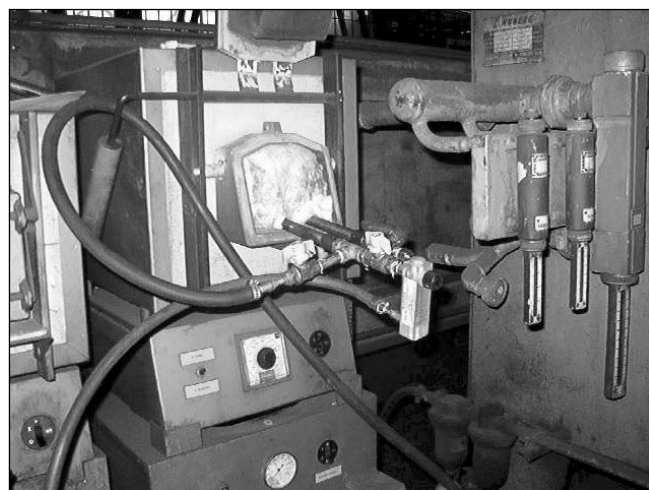


Fig. 3 – Laboratory furnace with device for hyper baric carburisation.

Fig. 3 – Fornetto di laboratorio attrezzato per le prove di carburazione iperbarica.

steel. The final results have been: surface carbon content 0.80%; case depth 0.55 mm; inter crystalline oxidation absent.

CONCLUSIONS

The obtained results confirm the validity of the new process of hyper baric carburisation. The cause of the defects arising from the traditional technology have been eliminated and the modifications requested on the furnaces are not expensive. In some cases, maybe the new furnaces are even cheaper, both in the buying phase than in the running cost. The most innovation in the new technology may be so summarized:

1) Compared to vacuum furnace

No necessity of the vacuum or low pressure with consequent elimination of the vacuum pump and the leakage problems. Possibility to set up a fan in the carburising chamber for better uniformity in surface carbon and case depth. Introduction of Titanium shaving or sponge with the carburising load, The high affinity of Titanium with the oxygen avoids totally the inter crystalline oxidation, while in the low pressure process, it is not always so.

2) Compared to controlled atmosphere furnace

The hyper baric pressure in the furnace allows avoiding contamination of the carburising atmosphere by the air through the leakage.

The saving of a continuous flow of endogas make the furnace more similar to the vacuum, whether for flexibility or for environment protection.

The introduction, with the carburising load, of Titanium shaving or sponge, avoids totally the inter crystalline oxidation, while in the controlled atmosphere that is not possible.

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CEMENTAZIONE CARBURANTE IPERBARICA

Parole chiave:
acciaio, carburazione,
trattamenti termici, impianti e attrezzature

Una nuova tecnologia (patented) che migliora la cementazione in bassa pressione nei forni a vuoto e la cementazione in gas nei sealed quench.

La diffusione a livello industriale della cementazione a bassa pressione si è ormai ritagliata una fetta di mercato. Essa presenta l'indubbio vantaggio sull'atmosfera controllata d'essere meno inquinante. Altri vantaggi vantati dai costruttori sono di meno facile riscontro come dimostra molta pubblicistica nata sull'argomento.

Tralasciando alcuni argomenti di carattere più commerciale come costi di produzione, velocità di carburazione, costi degli impianti, le discussioni più stimolanti riguardano le caratteristiche tecnologiche del prodotto rispetto a quelle ottenute con la vecchia tecnologia dell'atmosfera controllata.

Gli argomenti più controversi riguardano la resistenza a fatica e la resilienza, condizionate da:

- Impoverimento superficiale di elementi leganti.
- Ossidazione intercristallina.
- Drasticità di tempra con miscele varie di gas e pressioni

fino a 20 bar.

Si veda a questo proposito la bibliografia al fondo di questa memoria ai numeri 1), 2), 3).

Traendo spunto da questi argomenti si è voluto esaminare da un punto di vista scientifico quali sono i limiti ed i vantaggi sia del processo in bassa pressione che di quello iperbarico e valutare le possibilità tecnologiche del superamento di alcuni di questi limiti che condizionano le caratteristiche meccaniche del prodotto cementato e temprato.

Per proporre delle soluzioni tecnologiche nuove che uniscano ai vantaggi di un processo ecologicamente "pulito" delle caratteristiche metallurgiche migliori vengono quindi dapprima esaminati:

- A Gli equilibri delle fasi solido - gas dei metalli ad alta temperatura.
- B Gli equilibri termodinamici dell'ossidazione intercristallina superficiale che avviene durante la cementazione con endogas o nei forni a vuoto che hanno perdite di vuoto eccessive.
- C I problemi che nascono dalla tempra in gas che essendo meno drastica di quella in olio, malgrado tutti gli accorgimenti fino ad oggi inventati, genera un decadimento delle caratteristiche meccaniche compresa quella particolarmente critica della resilienza. Vedasi studio di Fermand Da Costan 3) già citato.