

Finally, the sulphides are often the consequence of the calcium treatment applied in order to modify the oxide inclusions, but the little and finely dispersed CaS highly refractory inclusions can be detrimental for the casting procedure (nozzle clogging) and for the damaging effect. On the contrary the MnS non-metallic inclusions (often modified by the combination with CaS) are exploited for improving the cutting tool workability. In this case the MnS non-metallic inclusions are intentionally formed within the metal matrix in order to make the chipping brittle^{7,8,9} during the tool working. This role implies that the volume fraction of the non-metallic inclusions has to be significant and this aspect is the reason that excludes the application of EN10247:2003 for the estimation of the cleanliness of such a class of steels.

The formation and the control of the chemical composition of the non-metallic inclusions involve the different steps of the production processes and the industrial systems through which they are performed. The production process has to be carefully implemented in each step in order to avoid problems related to:

- difficulties during the casting operation associated with the nozzle clogging between the tundish and the mould (continuous casting system) and between the ladle and the casting column (ingot casting);
- detrimental effect on the mechanical properties of the steel.

The damaging effect of non-metallic inclusions

Three main mechanisms have been recognized at the origin of the non-metallic inclusion which are related to the damaging effects played by these non-metallic phases against the metal matrix^{10,11}. These mechanisms consider the non-metallic inclusions as:

- a) notching elements which amplify the stress field around the non-metallic inclusions;
- b) pressurized tanks of gas which progressively migrates into the non-metallic inclusions generating a stress field around the non-metallic inclusions;
- c) non-metallic phases which generate a residual stress due to the different thermal expansion coefficient associated to the metal phase and the glassy-ceramic ones.

The (a) mechanism is associated to a ductile process of crack formation which develops starting from the interface between the non-metallic inclusions and the steel. The voids are the precursor of cracks and on a macroscopic level the cooperative detrimental effect related to the voids formed by a large number of non-metallic inclusions produces a decrease of the ultimate tensile strain value which can be estimated as:

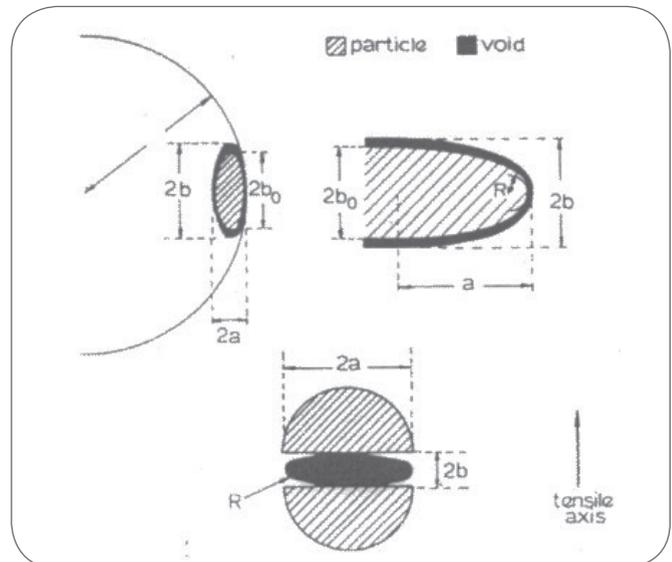
$$\varepsilon_t = \varepsilon_0 + 0,5 * \ln \left[\frac{(F^2 / f^2) + (k / r^2)}{1 + (k / r^2)} \right] \quad (1)$$

$$\varepsilon_t = \varepsilon_0 + 0,5 * \ln \left[1 + \frac{4r^2 F^2}{9kf^2} \right] \quad (2)$$

where

- ε_0 strain at the initiation void nucleation
- ε_t ultimate strain value at the fracture
- F critical void volume fraction associated with catastrophic failure
- f volume fraction of the non-metallic inclusions
- k stress amplification factor associated to the interface curvature
- r ratio b/a (ref. Fig. 2).

Relation (1) refers to the process of nucleation of the voids on the interface of the non-metallic inclusions while (2) describes the ultimate strain due to void nucleation caused by the fracture of



▲
Fig. 2

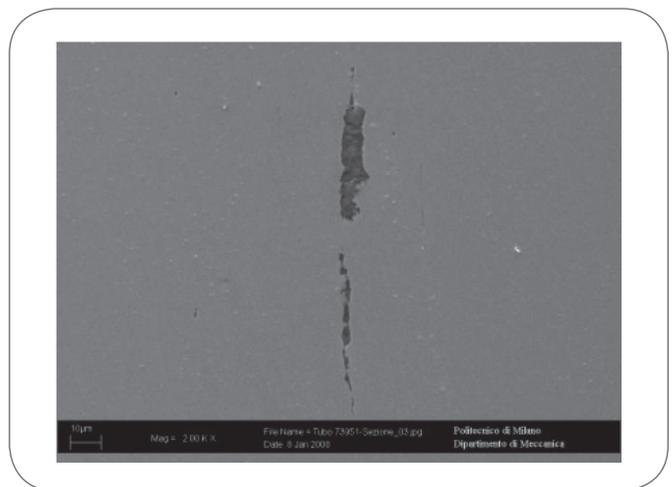
Development of voids at the interface between the non-metallic inclusions and the steel.

Sviluppo di vuoti all'interfaccia tra la matrice metallica e l'inclusione non metallica.

the non-metallic inclusions (Fig. 2).

The shown relations clearly point out that the factors detrimentally influencing the toughness and the macroscopic ductility of the steels are: the increase of the volume fraction, the decrease of the curvature radius and the fracture of the non-metallic inclusions.

The coalescence among the nucleated voids is extremely dangerous because the voids of adjacent inclusions can coalesce to form a large crack, so the formation of elongated strips of non-metallic inclusions represents a very dangerous situation (Fig. 3). Thus, the non-metallic inclusions constituted by brittle ceramic phases which can form elongated fractured strips have to be carefully avoided.



▲
Fig. 3

Example of fractured strips of non-metallic inclusions.

Esempio di una "cometa" di inclusioni non metalliche fratturate.

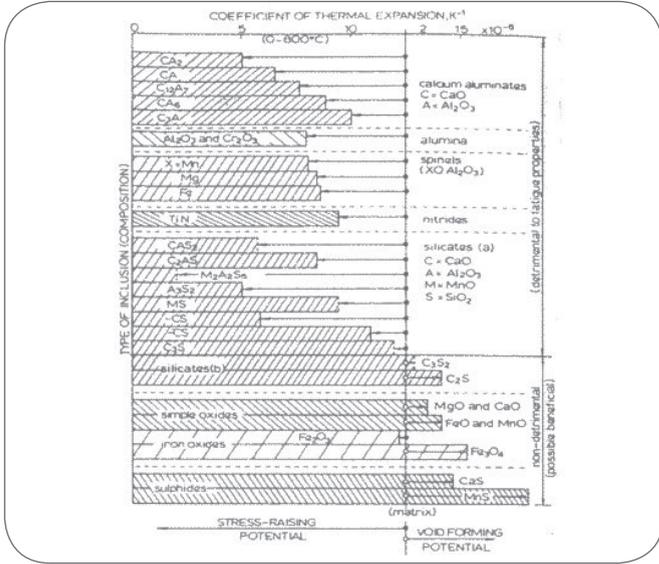


Fig. 4 Thermal dilation coefficients of the non-metallic inclusions compared with the iron one. *Coefficienti di dilatazione termica di alcune inclusioni non metalliche confrontati con quello del ferro.*

It is worth noting that the just described mechanism is featured by a ductile process on microscopic scale, but its effect on a macroscopic level turns out as a decrease of the toughness and of the ductility.

The (b) mechanism is related to the highest solubility shown for hydrogen by the sulphides:

$$[H] = K p_{H_2}^{0,5}$$

$$\log K = -1418 / T + 1,628$$

so, the inclusions become pressurized tanks pulling on the metal matrix and giving rise to a stress field which will be summed to the one formed by the external force applied during the service of the steel.

The (c) mechanism takes place as a consequence of the different thermal expansion coefficient featuring the steel and the glassy and/or ceramic structures characterizing the non-metallic inclusions (Fig. 4).

The silicates, the aluminates and generally all the oxides (except CaO and MgO) have a thermal expansion coefficient lower than one of the steel metal matrix, while the sulphides are featured by a contrary behaviour.

The detrimental action is due to the residual stress generated on the interface between the inclusions and the metal matrix (Fig. 5, Fig. 6). In fig. 6 is clear the dangerous stress combination which can cause also the initiation of a damaging fatigue crack.

The higher the size of the non-metallic inclusion the larger is the detrimental effect, so in order to prevent this mechanism the limitation of the size of a non-metallic inclusion is a fundamental aspect while the overall volume fraction of the inclusional population does not play a significant role in this mechanism.

A classification for what has to be considered a macro-inclusion has not been defined in any standard. On the other hand this information can be extremely difficult to be provided, because for a round shape inclusion a diameter of 14-20µm can be dangerous, but for edged inclusions (i.e. TiN) the dangerous size can be stated even at a lower level (2-4µm) as a consequence of the

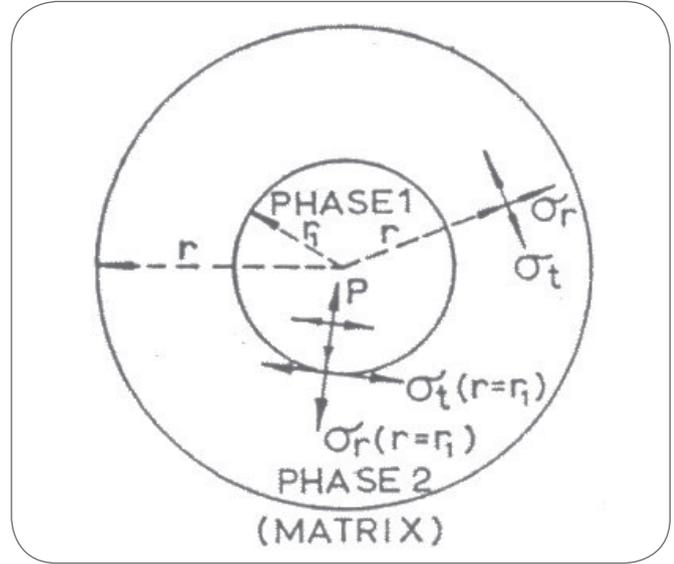


Fig. 5 Stress field developed around a round non-metallic inclusions as a consequence of the different thermal dilation between the non-metallic material and the steel. *Campo di sforzo sviluppato in prossimità dell'inclusione non metallica come conseguenza del differente coefficiente di dilatazione termica tra l'inclusione stessa e la matrice metallica.*

higher stress amplification associated to the edged shape. The treatment of this aspect is further complicated by the fact that the danger level can be strongly affected by the configuration of the non-metallic system which is ruled by the chemical composition of the participating phases. Actually, a correct engineering of the non-metallic inclusions could permit to realize a sulphide crown precipitated on an oxide core and this system configuration mutually compensates the expansion coefficient of the non-

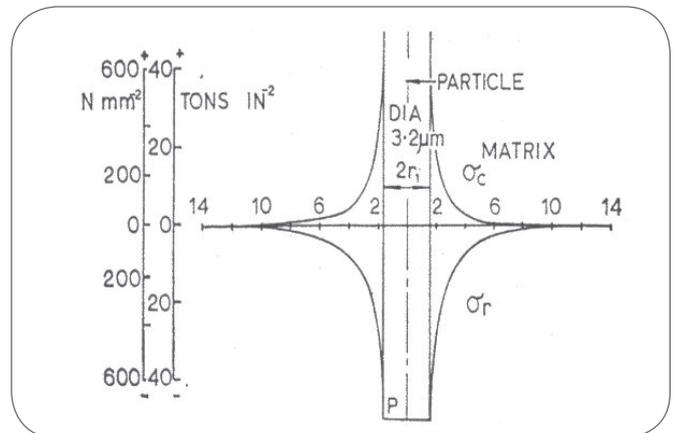
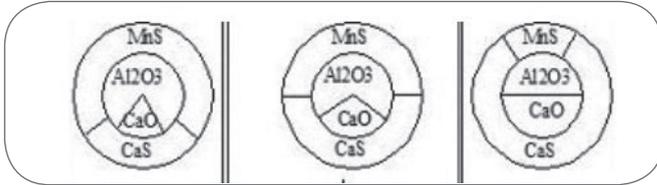
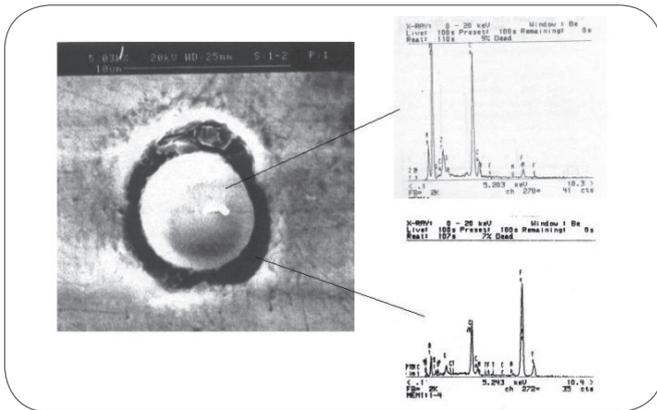


Fig. 6 Trend of the stress field around the non-metallic inclusions as a function of the distance from the non-metallic inclusions boundary. *Andamento del campo di sforzo generato in prossimità dell'inclusione non metallica in funzione della distanza dal bordo della stessa.*



▲
Fig. 7

Example of layout of the non-metallic inclusions with an oxide core and a surrounding sulphide crown.
Schema della configurazione di inclusioni non metalliche con un cuore a base di ossido ed una corona di solfuro di manganese.



▲
Fig. 8

An example of a non-metallic inclusions featured by an oxide core and a surrounding sulphide crown (Mapelli-Vedani-Zoppi).
Esempio di inclusione non metallica con cuore di ossido e corona circostante a base di solfuro (Mapelli-Vedani-Zoppi).

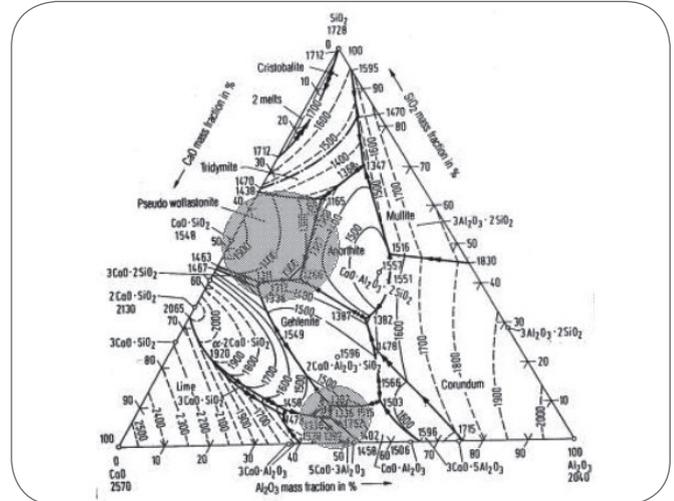
metallic phases, approximating the one of the steel metal matrix (Fig. 7-Fig. 8).

The origin and modification of non-metallic inclusions in secondary metallurgy

The formation of the non-metallic phases is ruled by the thermodynamic relations. The oxide system represents the most difficult one to be studied because of the presence of different oxide species. Moreover, the insertion of Ca aiming at the modification of the non-metallic inclusions makes even more difficult the understanding of the interaction interesting the steel bath. A good procedure for the engineering of the non-metallic inclusions aimed at developing low melting non-metallic oxides - in order to avoid the nozzle clogging - and at maintaining a prevalently glassy structure of the non metallic inclusions during the steel cooling and the successive heating imposed to perform the plastic deformation -in order to avoid the formation of ceramic brittle phases - (Fig. 9, Fig. 10). The need to stabilize the glassy structure makes interesting the formation of silicate system based on the presence of anorthite and pseudo-wollastonite which appears to be particularly favourable.

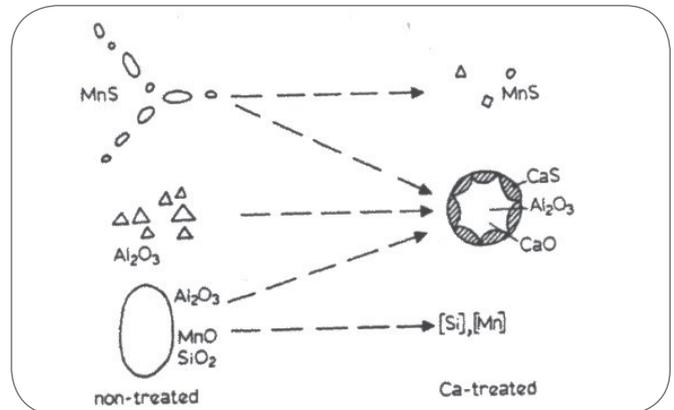
The prediction and the engineering of the non-metallic oxide inclusions can be based on a powerful and simple thermodynamic model¹²⁾ for the prediction of the non-metallic inclusions can be divided into three main steps:

- computation of the oxygen potential associated with the slag;
- evaluation of the possibility of the development of the reactions



▲
Fig. 9

The two regions on the ternary diagram featured by inclusions characterised by a low melting point.
Diagramma ternario in cui sono state evidenziate le inclusioni non metalliche caratterizzate da un basso punto di fusione.



▲
Fig. 10

Modification of the non-metallic inclusions performed by Ca-treatment (Gaye et al.).
Schema generale di azione del calcio nella modifica delle inclusioni non metalliche (Gaye et al.).

to create some pure non metallic compounds;
- definition of a hierarchy of the different reactions as a function of the associated oxygen potentials on the basis of the chemical composition of the steel.

The first step is related to the determination of the upper limit of the oxygen activity which can feature the steel bath. The upper limit of the oxygen potential available for the reactions which can take place within the bath has been computed through the model proposed by Ohta et al.¹³⁾. The slag can be considered as containing a tank of oxygen available for the development of the oxidation reactions which take place in the steel. The activity coefficient of the iron oxide contained in the slag has been computed on the basis of the other non metallic compounds contained in it:

$$(3) \log \gamma_{FeO} = \frac{0.676 \cdot \%MgO + 0.267 \cdot \%Al_2O_3 - 19.07}{\%SiO_2} + 0.0214 \cdot \%CaO - 0.047$$

The FeOx activity has been computed through the product between the molar concentration of this species and the computed acti-

vity coefficient (3). The upper limit of the oxygen activity (ad so of the related oxygen potential) available for the steel bath has been derived from the equilibrium constant¹³) that has been demonstrated to be a reliable tool to determine the oxygen equilibrium between the slag and the melt:

$$(4) \log_{10} \frac{[a_O]}{(a_{FeO_x})} = -\frac{6320}{T} + 2.765$$

The second step is focused on the evaluation about the thermodynamic possibility of the formation of the non-metallic compounds. The formation of the non-metallic compounds is considered possible only when their related oxygen activity of equilibrium is lower than the upper limit imposed by the slag. The reactions for the formation of the non-metallic compounds which can represent a complete enough set of oxide system is:

- (5) $[Ca] + [O] \rightarrow < CaO >$
- (6) $3[Al] + 2[O] \rightarrow < Al_2O_3 >$
- (7) $[Si] + 2[O] \rightarrow < SiO_2 >$
- (8) $< Al_2O_3 > + 3[Ca] + 3[O] \rightarrow < 3CaO.Al_2O_3 >$
- (9) $2 < Al_2O_3 > + [Ca] + [O] \rightarrow < CaO.2Al_2O_3 >$
- (10) $7 < Al_2O_3 > + 12[Ca] + 12[O] \rightarrow < 12CaO.7Al_2O_3 >$
- (11) $2[Si] + < Al_2O_3 > + 4[O] \rightarrow < 2SiO_2.Al_2O_3 >$
- (12) $2[Si] + 3 < Al_2O_3 > + 4[O] \rightarrow < 2SiO_2.3Al_2O_3 >$
- (13) $[Si] + < Al_2O_3 > + 2[O] \rightarrow < SiO_2.3Al_2O_3 >$
- (14) $[Si] + [Ca] + 3[O] \rightarrow < SiO_2.CaO >$
- (15) $[Si] + 2[Ca] + 4[O] \rightarrow < SiO_2.2CaO >$
- (16) $[Si] + 3[Ca] + 5[O] \rightarrow < SiO_2.3CaO >$
- (17) $2[Si] + 3[Ca] + 7[O] \rightarrow < 2SiO_2.3CaO >$
- (18) $2[Si] + < Al_2O_3 > + [Ca] + 5[O] \rightarrow < 2SiO_2.CaO.Al_2O_3 >$
- (19) $[Si] + < Al_2O_3 > + 2[Ca] + 4[O] \rightarrow < SiO_2.2CaO.Al_2O_3 >$
- (20) $2 < SiO_2 > + < Al_2O_3 > + [Ca] + 4[O] \rightarrow < 2SiO_2.CaO.Al_2O_3 >$
- (21) $< SiO_2 > + < Al_2O_3 > + 2[Ca] + 2[O] \rightarrow < SiO_2.2CaO.Al_2O_3 >$
- (22) $< SiO_2 > + 2[Al] + 3[O] \rightarrow < 2SiO_2.3Al_2O_3 >$
- (23) $< SiO_2 > + [Ca] + [O] \rightarrow < SiO_2.CaO >$
- (24) $< SiO_2 > + 2[Ca] + 2[O] \rightarrow < SiO_2.2CaO >$
- (25) $< SiO_2 > + 3[Ca] + 3[O] \rightarrow < SiO_2.3CaO >$
- (26) $2 < SiO_2 > + 3[Ca] + 3[O] \rightarrow < 2SiO_2.3CaO >$
- (27) $< MgO > + 2[Al] + 3[O] \rightarrow < MgO.Al_2O_3 >$
- (28) $[Mg] + 2[Al] + 4[O] \rightarrow < MgO.Al_2O_3 >$
- (29) $< MgO > + 2[Al] + 3[O] \rightarrow < MgO.Al_2O_3 >$
- (30) $< SiO_2 > + < Al_2O_3 > + [Ca] + 4[O] \rightarrow < SiO_2.CaO.Al_2O_3 >$
- (31) $3 < SiO_2 > + < Al_2O_3 > + 3[Ca] + 3[O] \rightarrow < 3SiO_2.3CaO.Al_2O_3 >$
- (32) $[Si] + < Al_2O_3 > + [Ca] + 6[O] \rightarrow < SiO_2.CaO.Al_2O_3 >$
- (33) $3[Si] + < Al_2O_3 > + 3[Ca] + 9[O] \rightarrow < 3SiO_2.3CaO.Al_2O_3 >$

and each variation of the Gibbs free energy associated to their development has been computed on the basis of the Gibbs free energy of each chemical species involved in the reactions^{14,15}) (Tab. 1). Then, the constants of equilibrium of each reaction have been computed by the variation of the Gibbs free energy determined through the difference among the energies of the right side compounds and the left side ones.

The activity of each alloying element present in solution has been obtained through the Wagner formalism¹⁶) for a system including Fe-Si-Mg-Al-Ca-O:

$$(34) a_B = \gamma_B^0 X_B + X_B \exp(\epsilon_B^B X_B + \epsilon_B^C X_c + \dots + \epsilon_B^N X_n)$$

while the equilibrium activity of the oxygen for each reaction has

| Chemical species | G° (J/mol) |
|--|-----------------|
| Si | -58.9T+30004 |
| Ca | -99.2T+44799 |
| Al | -84.2T+42591 |
| Mg | -136T+98253 |
| O | -145.2T-76028 |
| CaO | -117.6T-580918 |
| SiO ₂ | -134.5T-848440 |
| Al ₂ O ₃ | -235.2T-1539859 |
| 3CaO.Al ₂ O ₃ | -601T-3312118 |
| CaO.2Al ₂ O ₃ | -586T-3710542 |
| 12CaO.7Al ₂ O ₃ | -3173T-17894624 |
| 2SiO ₂ .Al ₂ O ₃ | -523.3T-2946164 |
| 2SiO ₂ .3Al ₂ O ₃ | -992.6T-6273164 |
| SiO ₂ .CaO | -256.4T-1463400 |
| SiO ₂ .2CaO | -364.2T-2069624 |
| SiO ₂ .3CaO | -507.5T-2643282 |
| 2SiO ₂ .3CaO | -628.6T-3533520 |
| 2SiO ₂ .CaO.Al ₂ O ₃ | -636T-3913789 |
| SiO ₂ .2CaO.Al ₂ O ₃ | -612T-3700167 |
| 3SiO ₂ .3CaO.Al ₂ O ₃ | -911T-6187916 |
| SiO ₂ .CaO.Al ₂ O ₃ | -479T-3063983 |
| MgO | -235.2T-1539859 |
| MgO.Al ₂ O ₃ | -326T-2139278 |

▲
Tab. 1

Gibbs free energy at standard states for the chemical species included in the studied system.

Energie libere di Gibbs allo stato standard per la specie chimiche considerati nelle reazioni.

been evaluated through the associated constant of equilibrium. The activities of Al₂O₃, SiO₂ involved as reactants in the reactions have been taken with the values computed in reactions (6) (7) at the beginning of the LF treatment, provided the measured oxygen activity and the computed activities of Al and Si. The MgO has been considered as a pure phase, because it is present in this state in the refractory lining of dolomia and magnesia, so its activity has been stated at 1.

An efficient computational procedure which can be followed to run the model and it can be briefly described through several few steps:

- the species produced by each reaction has been taken with an activity of 1, because this condition grants the formation of the produced phase as pure and separated from the steel, although the produced phase stays within the volume of the steel bath;
- the activity of the reactants has been computed through the chemical composition of the steel and through the Wagner formalism exploiting the activity coefficient and the interaction ones;
- the oxygen activity associated with the slag composition has been computed through (3) and (4) and compared to the ones associated with each specific reaction at a particular temperature;
- the reactions featured by an equilibrium oxygen activity lower than the one imposed by the slag has been considered as possible and their development is allowed by the presence of an available



▲
Fig. 11

An example of pure Al_2O_3 non metallic inclusions revealed just after the first deoxidation operated through the Al addition.

Esempio di inclusione di allumina prodottasi nell'acciaio dopo la prima disossidazione allo spillaggio dal forno elettrico.

thermodynamic driving force that can be expressed as:

$$(35) \Delta G = RT \ln \frac{(a_O)_{slag}}{[a_O]_{reaction}} < 0$$

- the possible products formed as pure phases after the first deoxidation (i.e. Al_2O_3 , SiO_2) are applied in the following steps as the reactants in the reactions in which they are included under this role, otherwise those reactions have to be excluded from the computation for the lacking of the needed reacting phases;

The final results are represented by the reactions featured by a negative value of (35) and their tendency to the development is greater as the associated driving force is larger.

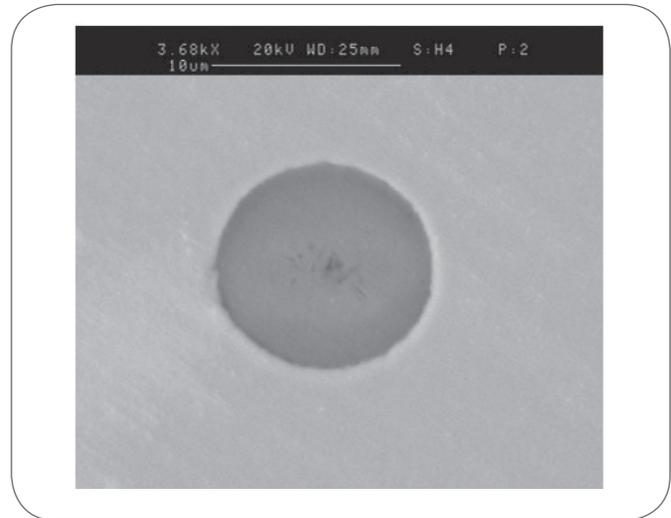
The industrial experimental trials and the discussion performed by the thermodynamic approach have permitted to state that:

- the formation of the complex silicates of Ca and Al (i.e. pseudowollastonite, anorthite, grossularia etc.) is made possible only in the steels which have been treated through a sequence of alloying additions which permit to realize a higher activity of the silica before the Ca addition; generally this condition can be reached only through the insertion of Si as a deoxidant with Al just after the tapping from EAF;

- the deoxidation performed by the use of Al permits the formation of only gehlenite as the complex silicate of Al and Ca. This compound has always been observed in the steel grades deoxidised through Al and in the ones deoxidised also by Si, because also according to the developed computational model its formation does not need the presence of a high silica activity and it can be produced by the reaction of solved Si and Ca with the oxygen and the developed pure alumina;

- the deoxidation through the use of only Al causes the prevalent presence of $SiO_2 \cdot 2CaO \cdot Al_2O_3$, $3SiO_2 \cdot 3CaO \cdot Al_2O_3$, $SiO_2 \cdot CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$, $12CaO \cdot 7Al_2O_3$ (Fig. 11, Fig. 12, Fig. 13). From the model forecasting and on the basis of the performed experimental observation the presence of the extremely favourable $12CaO \cdot 7Al_2O_3$ seems to be favoured by the %Al/%Ca included in a range between 18 and 22. An excess in the use of Ca has to be avoided not to worsen the cleanliness of the steel;

- the spinel ($MgO \cdot Al_2O_3$) has never been observed as a pure phase



▲
Fig. 12

Example of an anorthite inclusion found in a steel at the end of the LF treatment.

Esempio di inclusione di anortite trovata in un acciaio al termine del trattamento in LF.

and from the information provided by the computational model it can be formed or during the first deoxidation procedure or during a local reoxidation event. However, it is interesting to observe that a variable quantity of Mg (1-2%) has been detected in the core of the non-metallic inclusions. This observation suggests that the $MgO \cdot Al_2O_3$ inclusions can behave as a nucleant phase for the other non-metallic compounds.

The desulphurisation procedure applied to the steel aims at decreasing the presence of S in a quantity low enough to certainly avoid the formation of the eutectic FeS. A good and efficient desulphurisation procedure is based on high index of slag basicity, strongly deoxidized bath and high temperature range (1620-1640°C). On the other hand, the resulphurised steel grades have known a progressively large success at the end of '90s of the XX centuries for the replacement of leaded steel and the realization of efficient free cutting steels. The production of resulphurised steels aimed at the precipitation of MnS, whose nucleation and growth has to be promoted during casting by the precipitation in the interdendrite spacings. On the other hand, particular attention has to be paid in order to avoid the strong precipitation of sulphide and oxides due to a non-correct design of the production route. Actually, especially in the production of continuously cast resulphurised steels the calcium treatment is always applied for the usual modification of the oxide non-metallic inclusions as well as to exploit the favourable formation of complex (Mn.Ca)S inclusions which have a lower tendency to elongate along the flow direction imposed by the plastic deformation (Fig. 14)¹⁷.

But such a procedure implies also a risk for the steelmaking management, because after the final addition of the sulphur to the steel bath, it cannot be longer re-heated, otherwise the reaction:



shifts toward the right side producing a re-oxidation of the steel bath and the simultaneous formation of inclusions produced by the already present deoxidising elements (i.e. Al, Si, Ca et.) and the contextual precipitation of undesired CaS inclusions which decrease the final tool workability of the steel and contribute to the nozzle clogging. About the reoxidation phenomena it is worth noting that one of the under-evaluated critical aspect in the formation of the

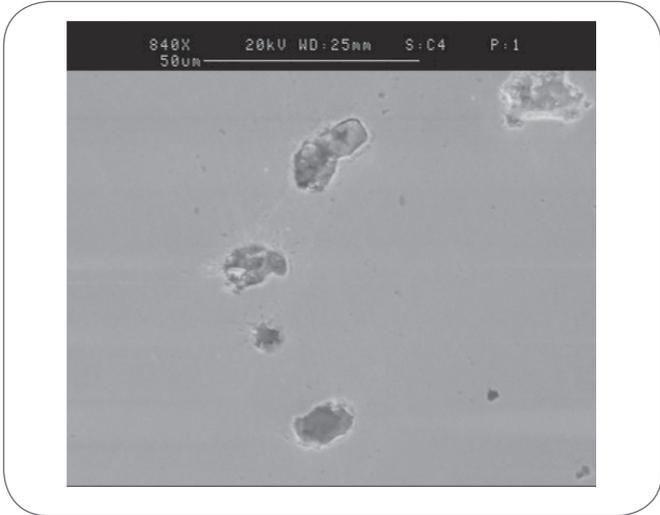


Fig. 13 An example of some inclusions rich in $\text{SiO}_2 \cdot 2\text{CaO} \cdot \text{Al}_2\text{O}_3$ (gehlenite) found after deoxidation through Al. Esempio di alcune inclusioni ricche in $\text{SiO}_2 \cdot 2\text{CaO} \cdot \text{Al}_2\text{O}_3$ (gehlenite) riscontrate a seguito della disossidazione con alluminio.

non-metallic inclusions is represented by the oxygen level present in the iron-alloys which can be the source of transitory but strongly polluting re-oxidation in the steel bath.

The TiN non-metallic inclusions are particularly dangerous because of their edged shape which can strongly amplify the applied stresses (Fig. 15).

The TiN non-metallic inclusions can be fast recognized for their morphology and for the pink-colour typical of the nitride. The Ti addition is generally used for performing deoxidation and denitration, but the dangers associated to its application can be related to the persistent pollution of the steel heats refined in the same ladle furnace.

Decreasing of the volume fraction of the non-metallic inclusions

The decreasing of the overall content of non-metallic inclusions can be performed through

- the elimination of the reacting species (i.e. O, N, S) which are located on the anionic sites of the elementary cell featuring the non-metallic inclusions;
- the efficient removal of the non-metallic inclusions once they have been formed.

The decreasing of the detrimental solved oxygen before its combination with the alloying elements can be realized decreasing the oxygen content by the formation of gaseous compounds. This procedure can be followed for removing oxygen content just after tapping avoiding a deep deoxidation by precipitation. The delaying in the addition of deoxidising elements or the addition of solid graphite can allow the nucleation of CO bubbles, which decrease the concentration of solved oxygen by the formation of gaseous phases. Some industrial trials have proved the efficiency of such a process in order to improve the cleanliness of the steel (Fig. 16)¹⁸. This technique seems to be particularly suitable for the steel heats poured from the EAF with an oxygen content higher than 950ppm.

Instead, the method to remove the non-metallic inclusions from the liquid bath are prevalently based on the mass transport and so the variation of the volume fraction can be described by:

$$(37) \frac{N - N_\infty}{N_0 - N_\infty} = \exp\left(-\beta_p \frac{A_b}{V_b} t\right)$$



Fig. 14 Examples of strongly elongated non-metallic inclusions. Esempi di inclusioni a base di MnS fortemente allungate nella direzione imposta dalla deformazione plastica.

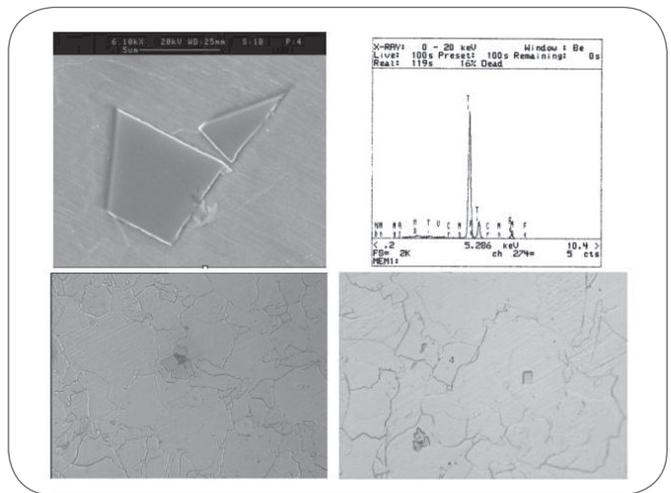


Fig. 15 Example of non-metallic TiN inclusions (by R. Venturini - 2004). Esempi di inclusioni di TiN (R. Venturini - 2004).

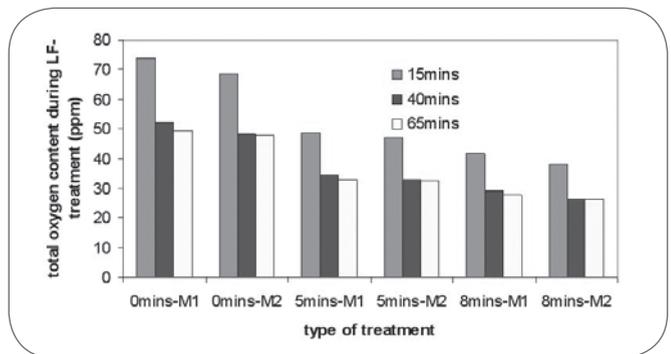
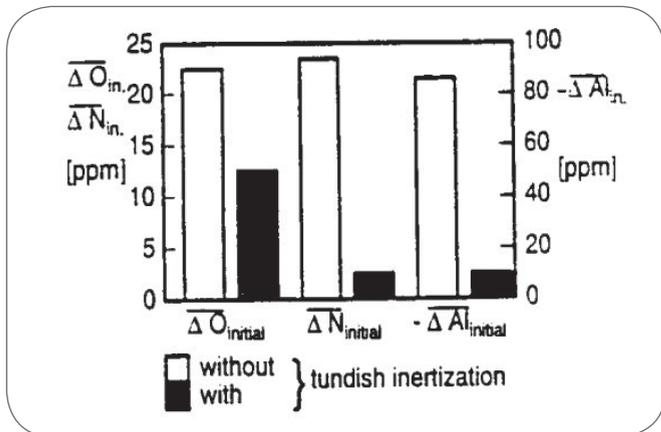


Fig. 16 Total oxygen content as a function of the delayed time of deoxidation after tapping and the volume rate of Ar bubbling M1 (140 l/min) and M2 (250 l/min). Contenuto totale di ossigeno in funzione del ritardo applicato dell'inserzione di alluminio a seguito dello spillaggio ed in funzione delle portate di Ar M1(140l/min) e M2 (250l/min).



▲
Fig. 17

Effect of tundish inertization on the oxygen, nitrogen and aluminium concentration (by Bannenberg).
Effetto dell'interizzazione della panierina sulla concentrazione di ossigeno, azoto ed alluminio contenuti nell'acciaio (Bannenberg).

where

N is the current number per unit volume at instant t (m^{-3})

N_0 is the initial number of non-metallic inclusions per unit volume (m^{-3})

N_∞ is the number of non-metallic inclusions per unit volume at infinite time (m^{-3})

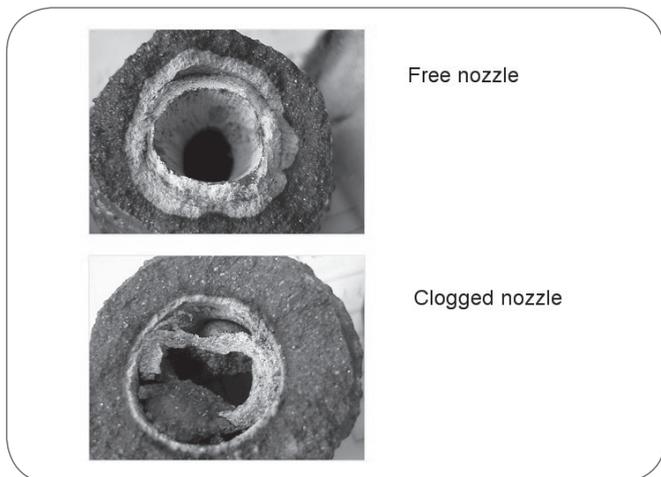
A_b area of the interface between the treated volume and the slag (m^2)

t is the time (s)

V_b volume of the treated steel (m^3)

β_p represents the transport coefficient (ms^{-1}).

The average value of transport coefficient estimated for LF is $6.5 \cdot 10^{-4}$ m/s, while for the tundish and mould the transport coefficient for the removal of the non-metallic inclusions has been stated at $4 \cdot 10^{-4}$ m/s. This variation is significant enough because it implies a variation of about 40% of the transport coefficient. This phenomenon can be explained by the higher rising motion imposed by Ar bubble plume introduced into the steel bath contained in the ladle through

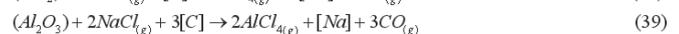
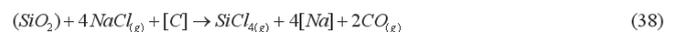


▲
Fig. 18

Example of a nozzle free from the non-metallic inclusions and an example of a clogged nozzle.
Esempio di tuffante libero dalle inclusioni non metalliche ed esempio di tuffante occluso dalle incrostazioni di inclusioni.

the bottom porous nozzles. The application of the same formalism in the case of induced CO effervescence can lead to an approximate overall value of the transport coefficient for the LF treatment, which is estimated in 0.07 m/s which is two order of magnitude larger than the previous ones, but it needs a correct interpretation. Actually, this strong increment of the transport coefficient should be attributed also to the rising movement produced by the nucleation of CO bubbles from the steel.

Another technique rarely applied in the industrial practice but successfully tested in the laboratory experiments is the introduction of chloride, fluoride and graphite to the steel, which permits to remove the non-metallic inclusions through the formation of gaseous species according to the relation:



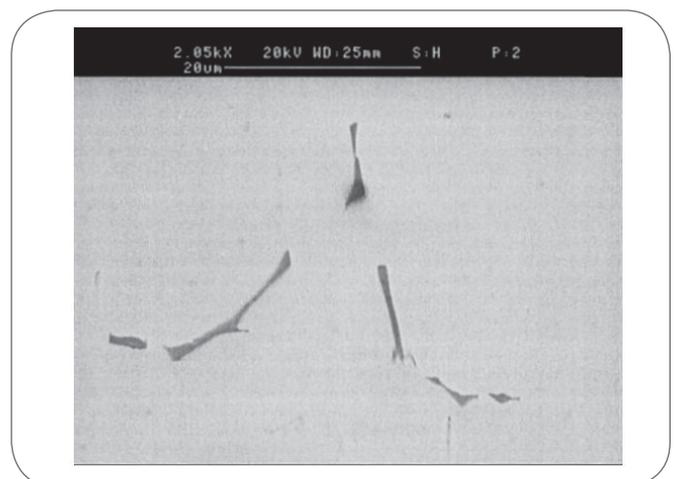
The criticalities related to such an approach are related to:

- the control of carbon content in the steel;
- the increase in the formation of dioxin compounds which can be decreased only by an efficient scrubbing system;
- the modality of introduction of the halides in order to avoid a too fast gasification which could not permit to perform a correct introduction and interaction with the whole liquid bath.

The non-metallic inclusions during solidification and continuous casting

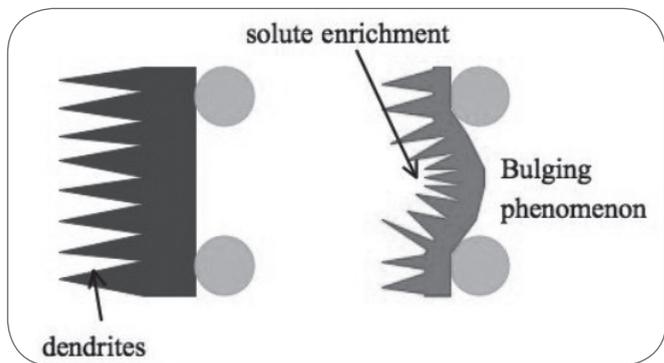
The control of the non-metallic inclusions during the casting operation involves the control of the fluid flow of the liquid phase, the clogging of the pouring nozzles and the generation of the non-metallic inclusions within the interdendrite spacings.

The fluid flow in the continuous casting involves the correct tundish design. The residence time in the tundish has to be maximized avoiding the realization of dead flowing volumes and the excessive wear of the refractory linings. This aim can be realized through the elimination of an excessive turbulence and the application of deflecting walls, which can make more homogeneous the distribution of the temperature drops among the different casting lines. An efficient control can reduce of about 80% the non-metallic fraction present in the steel poured from the ladle furnace. Another interesting action is related to the inertization of the tundish volume through



▲
Fig. 19

Example of TiN formed in the interdendrite spacings.
Esempio di inclusioni di TiN formate negli spazi interdendritici.



▲
Fig. 20

Bulging phenomenon and solute enrichment on the tip region of the dendrite.

Schema del fenomeno di spanciamento che si può verificare tra i cilindri della macchina di colata continua.

the atmosphere saturation by Ar (Fig. 17)¹⁹. The non-metallic inclusions formed in LF and in the tundish are responsible for the nozzle clogging (Fig. 18)²⁰. From the process point of view this represents the most detrimental consequence, because it implies the immediate stop of the casting procedure with a dangerous and expensive economic effect due to the decrease of the productivity. Instead, the production of ingot has to face the significant problem of trapping of exogenous inclusions, due to the wear of columns and the channels. In literature there is a large characterization of those non-metallic inclusions and of their effects, but less information are contained about the origin. A strong effect has to be recognized in the wear of mullite-based refractory operated by the calcium contained in the steels^{4,5}. The calcium activity can be significant (6-8ppm) although the calcium treatment is not applied, especially when there are high basicity slags designed to produce steels grades featured by a very low sulphur content.

The rising and covering powders can play also a role but the certainty and the scientific indication of their role are not completely clarified, although the large experimental characterization data. Particularly, what appears not certain is whether they are source of the non-metallic inclusions or they have an indirect effect related to:

- the modification of the movement of the non-metallic inclusions;
- the thermodynamic interaction with the metal bath, which modifies only the chemical composition of exogenous or endogenous inclusions already contained in the steel.

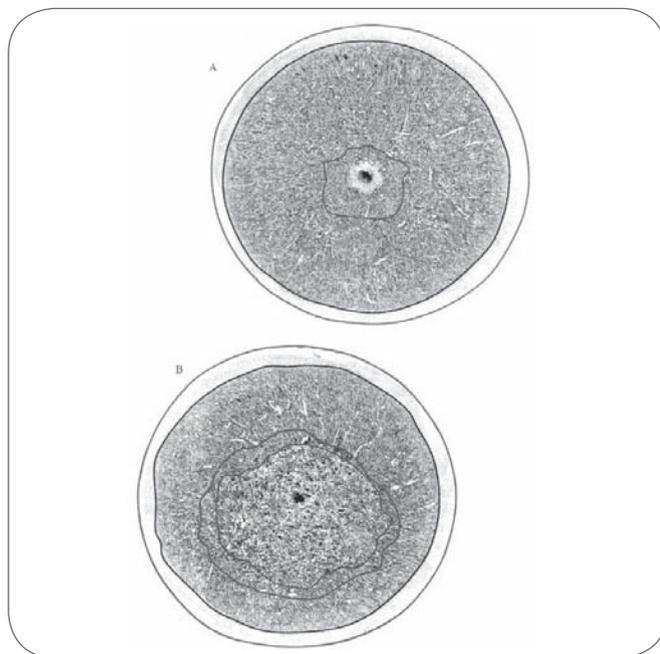
The development of MnS and the precipitation of dangerous edged TiN can be particularly strong also in the inter-dendrite spacings during the solidification of ingot and continuously cast products (Fig. 19).

This phenomenon is accentuated by the possible bulging during the continuous casting, which causes a large enrichment of segregating chemical species increasing the sizes fraction of the precipitated non-metallic compounds²¹ (Fig. 20).

The application of electromagnetic stirrers (EMS) can permit to produce a large equiaxed grain structure in the core of the continuously cast products, destroying the sharply defined alignment of the elongated non-metallic inclusions from the outer side to the centre of the semis²² (Fig. 21).

The stirrers do not cause a decreasing of the overall volume fraction of the non-metallic inclusions but they change their shapes, sizes and distribution avoiding or making the fracture event more difficult during the following operations of forging and more generally of plastic deformation.

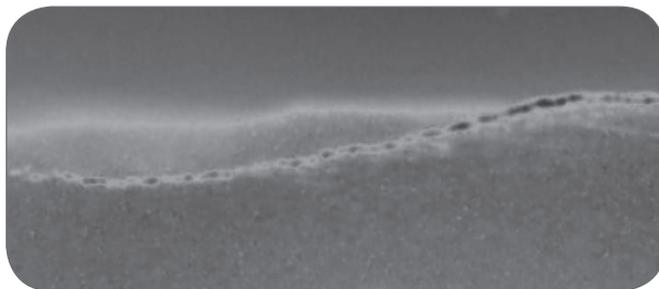
Finally, in the continuously cast semis the origin of subsurface non-



▲
Fig. 21

Different extension of equiaxed zone in non-stirred billet (A) and in the electromagnetically stirred billet (B). The difference in the alignment of the interdendrite segregation is evident.

Differente estensione della zona equiassica in una billetta non sottoposta ad agitazione elettromagnetica (A) e in una sottoposta a tale trattamento (B). E' evidente anche il differente grado di allineamento delle inclusioni non metalliche presenti nelle zone interdendritiche.



▲
Fig. 22

Example of surface defect induced by the interaction between the fluxes and the steel surface.

Esempio di difetti superficiali indotti dall'interazione tra la superficie dell'acciaio ed il flussante di lubrificazione.

metallic inclusions of exogenous origin can be due to the non-correct interaction of the lubricating flux which can generate an excessive pressure on the lubrication channel causing an increase of the non-metallic inclusions (Fig. 22). Several studies are performed in order to associate the characteristics of the fluxes with their consumption, the lubrication efficiency and the trapping of exogenous non metallic inclusions in the produced surface defects.

CONCLUSIONS

The information contained in this paper provides a landscape of the factors which influence the formation of the non-metallic inclusions

during the different steps of the steelmaking process. The design of the correct route has to be operated on the basis of the shown criteria, but the operative procedure cannot be a general and fixed scheme because each steelmaking unit has to perform a correct design as a function of the available plants and the mechanical requirements of the steels. In this sense the content synthetically exposed in this paper can constitute a brief guide-line in order to realize an efficient and clean process.

REFERENCES

- [1] J.C.C. Leach, Production of Clean Steel in Production and Application of Clean Steel, Iron and Steel Institute, London, 1970, 105-115.
- [2] F.B. Pickering, Effect of Processing Parameter on the Origin of non-metallic Inclusions in Production of Clean Steel in Production and Application of Clean Steel, Iron and Steel Institute, London, 1970, 75-92.
- [3] F. Oeters, Metallurgy of Steelmaking, Verlag Stahl Eisen, Dusseldorf, 1994, 54-98.
- [4] C. Mapelli, G. Cornacchia, M. Gelfi, A. Paderni, S. Panza, R. Roberti, ISIJ Int., 47, 3 (2007), 392.
- [5] 15. Lehmann, J., F. Bertrand, H. Gaye. La Revue de Metallurgie, 9 (1998), 1131-1139
- [6] Verein Deutsche Eisenhüttenleute, Schlackenatlas, Verlag Stahl Eisen, Dusseldorf, 1981.
- [7] M. Wakoh, T. Sawai, S. Mizogouchi, ISIJ Int., 36 (1996) 1014-1021.
- [8] H. S. Kim, H-G. Lee, W-G. Jung, ISIJ Int., 40 (2000), S82-S86.
- [9] K. Ramanujachar, S.V. Subramaniana, Wear, 197(1996), 45-55.
- [10] R. Kiessling, H. Nordberg, Influence of Inclusions on Mechanical Properties of Steel in Production of Clean Steel in Production and Application of Clean Steel, Iron and Steel Institute, London, 1970, 179-186.
- [11] T. Gladman: Ironmaking and Steelmaking, 19(1992), 457-463.
- [12] C. Mapelli, Steel Research Int., 7(2006), 462-471.
- [13] H. Ohta, H. Suito: Metallurgical and Materials Transaction B, 29B (1998), 119-129.
- [14] I. Barin, O. Knacke: Thermodynamical properties of inorganic substances, Springer Verlag, Berlin, 1973.
- [15] I. Barin, O. Knacke, O. Kubaschewski: Thermodynamical properties of inorganic substances, Springer Verlag, Berlin, 1977.
- [16] C. Bodsworth, H. B. Bell: Physical chemistry of iron and steel manufacture, Longman, London, 1972, 485-516.
- [17] M. Lahtinen, L.E.K. Holappa: Scandinavian Journal of Metallurgy, 19 (1990), 137-141.
- [18] L.F. Sancho, RFCS-PR-04140, 2nd Report-PREDINC, 2006.
- [19] N. Bannenberg, Revue de Metallurgie, (1995), 63-73.
- [20] C.E. Cicuti, J. Madias, J.C. Gonzales: Ironmaking and Steelmaking, 24 (1997), 155-159.
- [21] C. Mapelli, M. Vedani, A. Zamboni. Lat. Am. Appl. Res. v.32 n.3 Bahía Blanca jul./sept. 2002.
- [22] C. Mapelli, S. Baragiola, Ironmaking and Steelmaking, 33(2006), 379-388.

ABSTRACT

EFFECT OF HYDROGEN DIFFUSION ON ENVIRONMENTAL ASSISTED CRACKING OF PIPELINE STEELS UNDER CATHODIC PROTECTION

Parole chiave: acciaio, precipitazione, solidificazione, acciaieria, affinazione, colata continua, difettologia

La formazione delle inclusioni non metalliche coinvolge tutti gli stadi del processo produttivo siderurgico. Le inclusioni non metalliche possono essere classificate in base alla propria origine (endogene-esogene) ed in base alla loro composizione chimica (Fig. 1). La loro azione di danneggiamento sull'acciaio è legata al fatto che sono all'origine della nucleazione di vuoti che possono coalescere dando luogo ad una cricca (Fig. 2, Fig. 3) oppure sono in grado di generare degli sforzi residui sulla matrice metallica che si sommano ai carichi di esercizio e possono far insorgere delle cricche di fatica (Fig. 4, Fig. 5, Fig. 6). Quest'ultimo evento può essere limitato o evitato anche attraverso un'opportuna progettazione del ciclo produttivo che permette di generare inclusioni non metalliche caratterizzate da un cuore in ossido e da una corona di zolfo, in cui i coefficienti di dilatazione termica tendono a compensarsi (Fig. 7, Fig. 8). Per migliorare la colabilità dell'acciaio evitando problemi di otturazione dei sistemi di scarico e frattura delle inclusioni durante il processo di deformazione plastica una corretta progettazione delle inclusioni di ossido deve mirare alla formazione di inclusioni appartenenti alla regione della anortite, della pseudo-wollastonite e della mayanite (Fig. 9). Questo è l'obiettivo principale del trattamento con calcio (Fig. 10) che deve essere gestito correttamente e contestualmente alla disossidazione con Al e Si per consentire di pervenire alla formazione delle inclusioni desiderate (Fig. 11, Fig. 12, Fig. 13). Negli acciai risolforati il trattamento con calcio, se ben eseguito, dovrebbe avere anche lo scopo di formare inclusioni complesse (Mn.Ca)S che tendono a non allungarsi eccessivamente durante la deformazione plastica (Fig. 14), compromettendo l'affidabilità meccanica, in quanto tenderebbero a diminuire ulteriormente la sezione resistente in direzione perpendicolare a quella di allungamento e si caratterizzerebbero per fattori di amplificazione dello sforzo particolarmente gravosi. A questo riguardo risultano pericolose le inclusioni non metalliche a base

di nitruro di titanio (Fig. 15) caratterizzate da una forma particolarmente spigolosa. La diminuzione della frazione in volume di inclusioni non metalliche, con l'obiettivo della produzione di clean steel può trarre vantaggio da una corretta gestione della pratica di disossidazione, che si avvantaggi anche dei processi di effervescenza legati allo sviluppo di CO (Fig. 16), oppure all'impiego di tecniche piuttosto rare che però hanno dato luogo a significativi successi nella sperimentazione di laboratorio (relazioni da 38 a 41). L'operazione di colaggio è sempre un momento critico, anche e soprattutto in acciai che abbiano subito un trattamento sotto vuoto, poiché è spesso associata a gravosi fenomeni di riossidazione e riniturazione. Le pratiche di inertizzazione delle paniere dei sistemi di colata continua possono comportare favorevoli effetti (Fig. 17) anche volti a limitare problemi di occlusione del tufo (Fig. 18). Lo sviluppo delle inclusioni durante il processo di colata continua si localizza prevalentemente nella regione degli spazi interdendritici (Fig. 19, Fig. 20), in cui si possono formare inclusioni allungate e spigolose dovute a fenomeni di microsegregazione che possono essere accentuati dalla presenza di bulging (spanciamento) tra i cilindri. In particolare, possono risultare pericolosi i marcati allineamenti inclusionali che si verificano in strutture colonnari a forte direzionalità (Fig. 21) a cui si può rimediare con quei provvedimenti (bassi super-heat di colaggio, applicazione di agitatori elettromagnetici) che promuovono la formazione della zona equiassica centrale. Inclusioni di natura esogena durante il colaggio sulla macchina di colata continua possono interessare gli strati sub-superficiali del semilavorato, a causa dell'interazione fra il flussante di lubrificazione e la pelle calda sottile che si sta formando nel cristallizzatore (Fig. 22), mentre per quanto concerne il colaggio dei lingotti, anche se le polveri di risalita e copertura possono partecipare certamente alla modifica della composizione chimica delle inclusioni non metalliche già presenti nella massa, non esistono in letteratura su un campione statisticamente significativo di casi che possano far risalire direttamente alle polveri l'origine di inclusioni esogene; le polveri possono infatti modificare fortemente il processo di estrazione delle inclusioni non metalliche, modificando la situazione fluido-dinamica generale, possono cambiare la composizione chimica delle inclusioni stesse, per scioglimento nel bagno metallico di specie chimiche contenute nella formulazione, ma è difficile formulare un meccanismo plausibile ed esteso che governi l'intrappolamento della polvere.