

**CONTROL OF COMPLEX INCLUSIONS
DURING METALLURGICAL TREATMENTS
ON LIQUID AND SOLID STEELS**

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ABSTRACT: Adequate physical and mechanical properties, for numerous steel grades, can be obtained only with a precise control of the composition, morphology and plasticity of oxide and sulphide inclusions that remain in the product. In liquid metal, the composition of complex inclusions can be monitored by appropriate deoxidation practice, calcium treatment and/or slag-metal reaction. Further transformation may occur during solidification or heat treatments prior to hot-rolling: reaction between oxides and sulphides, as well as recrystallisation of oxides. An analysis of these factors, and of tools (thermodynamic models and laboratory experiments) which have been developed to comprehend and control them is presented.

I - INTRODUCTION

The increasing demand for numerous steel grades with improved and regular mechanical properties has led steelmakers to devise complex treatments for the precise control of the contents in non-metallic residuals (oxygen and sulphur, in particular), and of the composition of non-metallic inclusions (oxides and sulphides) that will remain in the solidified steel.

In general, the steelmaker will try to minimize the amount of oxide inclusions present in liquid steel before casting. As inclusions flotation is always imperfect, however, and as reoxidations from atmosphere, slags and refractories may occur, it is often advisable to adapt the treatments so that the resulting inclusions have a composition, morphology, plasticity such that they do not lead to problems of nozzle clogging, or affect metal shaping operations and product use. In other situations (free machining steels, for instance), it may be desirable to maintain a rather high content in oxide inclusions, but their composition has to be maintained in very narrow composition domains so that they retain a precise range of plasticity and can form protective layers on the cutting tool.

Some of these treatments consist in promoting reactions between liquid steel and top slag of appropriate composition in the ladle, and in introducing reagents (Ca, ...) in the liquid steel, in very precise amounts adapted as a function of steel composition and impurities level. A clear understanding and quantification of the reactions taking place during these treatments is an important asset for the definition of optimal operating conditions.

After solidification of the steel, the inclusions may undergo further transformations that will affect their behaviour at the shaping stage. Thus, reactions between oxide inclusions and sulphides which have precipitated around them during solidification can strongly modify their composition and mechanical characteristics. Oxide inclusions that had remained glassy in the cast product can recrystallize during the reheating stages prior to hot rolling.

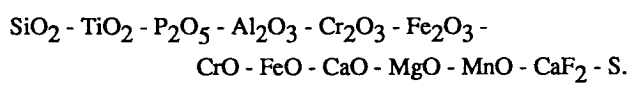
A description of experimental studies and thermodynamic models which have been developed with the aim of understanding these various phenomena and providing tools for the control of the process is presented.

**II - CONTROL OF THE COMPOSITION OF OXIDE
INCLUSIONS IN SECONDARY STEELMAKING**

Oxides control can be achieved either by equilibration of the liquid metal with a slag of well defined composition (industrial techniques are slag-metal stirring or flux injections), or by adding strong deoxidizers (e.g. Ca treatments) in amounts carefully adapted depending on steel grade and total oxygen content before treatment.

Various models for predicting the composition of oxide and sulphide inclusions that have precipitated as a result of these treatments, as well as defining optimum operating conditions, have been implemented. They are based on IRSID's slag (1) model for the representation of the thermodynamic properties of complex steelmaking slags.

The newest developments of the slag model, made through a cooperative research between IRSID and Nippon Steel Corp., have been presented in (2). They consist in an extension of the model formalism for the representation of oxi-sulphides and fluoride systems, as well as in extensions to additional oxide components (P₂O₅, Cr₂O₃, TiO₂). At present, the model provides a fairly accurate evaluation of the thermodynamic properties (component activities and phase diagrams) for complex compositions belonging to the system:



In particular, a marked improvement has been obtained for the

description of sulphur behaviour: the model provides a very reliable estimation for the sulphide capacity (whereas previous models (3) showed quite large discrepancies, in particular for slags containing FeO and MnO), as well as for the CaS solubility.

A specific procedure for the calculation of inclusions composition has been developed. Given the global analysis of a metal sample (that is, total Al, Mn, Si, Ca, Mg, ..., O, S contents), it consists in evaluating the composition and amounts of residual inclusions (oxides and sulphides) which may have been formed at treatment temperature and during the subsequent cooling until the steel starts solidifying. It assumes equilibrium between steel and inclusions as they precipitate. Since the first presentation of this procedure (4), it has been largely improved in order to increase its reliability and take into account the precipitation of solid oxides. The method makes use of a recurrent procedure for complex equilibria calculation, combining mass balance equations and equilibrium constraints. Starting from an approximate composition of the liquid oxide inclusions (which may be quite different from the equilibrium composition), the scheme consists in a "search pattern" which progressively modifies the composition of the oxides in order to equate all the oxygen activities corresponding to the equilibrium between the oxide components and the corresponding metal solutes. At each step of the search routine, the possible precipitation of sulphides (solid solutions of CaS - MnS) is checked. As it very closely oriented towards the description of the actual physical situation, this procedure converges quite reliably, and it is much less time consuming than the application of standard complex equi-

bria calculation codes. For instance, a typical calculation time is a few seconds CPU on IRSID's VAX 6320, whereas the same calculation can take a substantial number of minutes when using a procedure based on the SOLGASMIX code (5).

The procedure can be used as a previsual calculation for defining the appropriate treatment conditions, or as a check of inclusions composition from final product analysis. It is quite general and has been largely used to evaluate results in several French steel plants for various deoxidation practices (calcium treatments on steels containing or not aluminum, Si-Mn deoxidized steels, ...) and various steel grades (carbon steels or stainless steels).

As a first example, Figure 1 summarizes results obtained on Ca-treated Al-killed steel grades (4,6). The theoretical calculation of inclusions composition has been made for a large number of samples, either taken during the elaboration or on the final product, and its result confronted to microprobe analyses of the inclusions, or to the analysis of inclusions extracted by non-aqueous electrolytic dissolution of the steel matrix. Selective chemical analyses of the extracted inclusions provide not only their global composition, but also allow identification and quantification of the various phases present: CaO and calcium aluminates, SiO_2 , Al_2O_3 , CaS, (Ca-Mn)S, AlN. Figure 1a shows the comparison of analysed and calculated amounts of oxidized aluminum fixed as Ca-aluminosilicates, for several steel grades with varied sulphur levels and total Al contents in excess of 150 ppm. The agreement is rather satisfactory: the difference between the two values do not exceed ± 5 ppm. The comparison for the amounts of

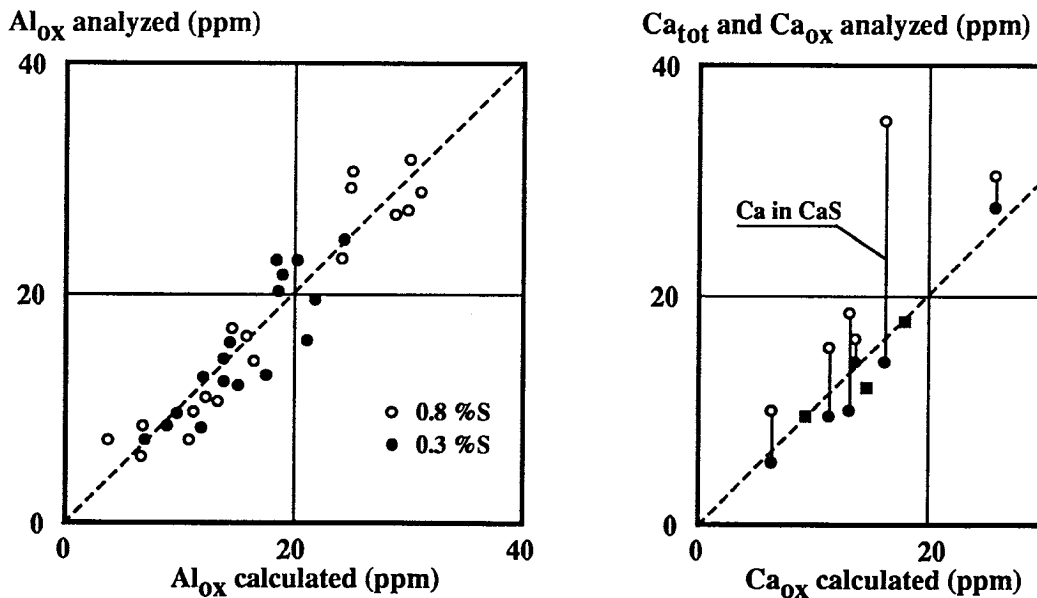


Figure 1: Comparison of computed distribution of Al and Ca between metal and oxide and sulphide inclusions with values analysed after electrolytic separation of inclusions.

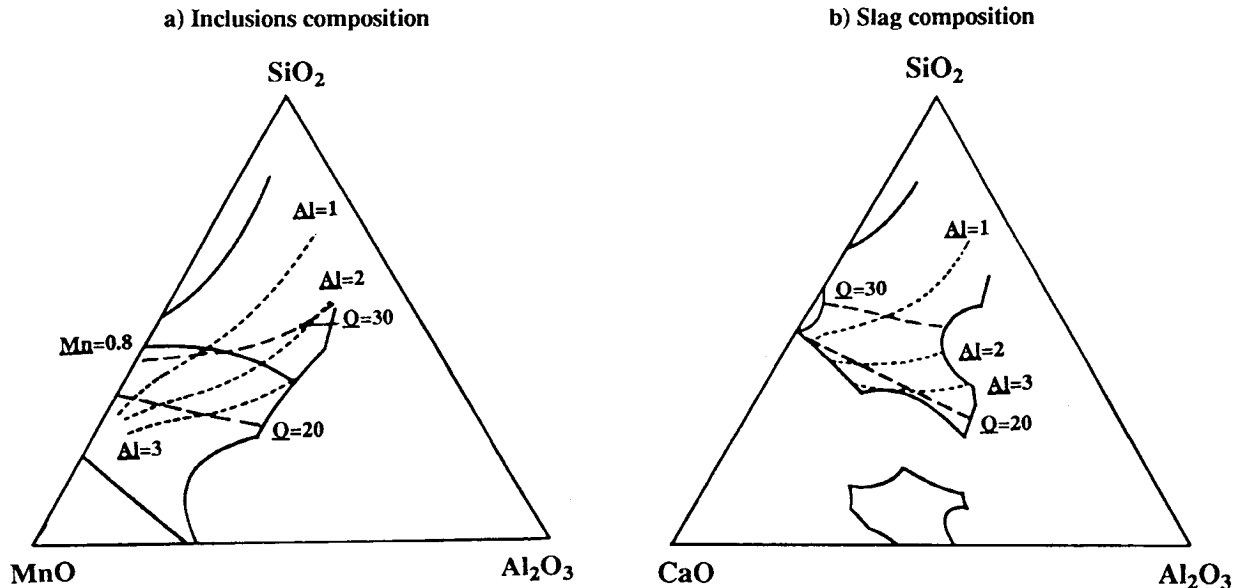


Figure 2: Use of the slag model to monitor inclusions composition via slag / metal reaction.
 (a) Inclusions composition in Si-Mn deoxidized steels as a function of residual contents in Al (ppm) and Q (ppm) at 1500°C .
 (b) Such low Al contents can be controlled through slag-metal equilibration.

calcium present as oxides or sulphides is shown on Figure 1b. Here again, the agreement is very satisfactory: for all samples in which calcium sulphide was analysed, and only for these samples, did the calculation predict the stability of the sulphide phase, and in about the right amount.

A second example concerns the elaboration of steelcord for which obtaining residual inclusions that will remain plastic during metal forming is a necessity. Adjusting the composition of these inclusions by controlled additions of strong deoxidizers (Al or Ca) is very difficult, as the contents in these elements compatible with inclusions in the desired composition domain (7) are very low. The results summarized in Figure 2 show that this adjustment can favorably be achieved by slag-metal equilibration. For a given steel grade (Mn and Si contents), the contents in residual Al and Q as a function of the composition of $\text{MnO-SiO}_2\text{-Al}_2\text{O}_3$ inclusions in equilibrium that will be precipitated upon deoxidation can be read on Figure 2a. It appears that Al content must remain very low in order to avoid the precipitation of alumina inclusions (less than 3 ppm at 1500°C , for instance, for a steel with 0.2 %Si and 0.8 %Mn). Such low contents can be achieved if the traces of aluminum brought by ferro-alloys are trapped in a slag of appropriate composition. The composition of such a slag can be fixed from the diagram of Figure 2b, by realizing the desired contents in Al and Q . During the subsequent slag-metal stirring, the composition of original oxide inclusions will be altered, as the metal aluminum content is decreased, and some replacement of MnO by CaO occurs. In order to obtain low-melting point inclusions, it is apparent that the

Al_2O_3 content of the slag should not exceed about 10 to 15%. This has been confirmed by industrial results obtained on this steel grade (8).

III - CHANGES IN THE COMPOSITION OF OXIDE AND SULPHIDE INCLUSIONS IN SOLID METAL.

The thermodynamic models can also be used to predict the composition of complex inclusions that precipitate during liquid metal cooling and solidification.

In Al-killed Ca-treated steels, for instance, the inclusions formed during the calcium treatment will be richer in CaO than those precipitating during liquid metal cooling and solidification (Figure 3). However, if reoxidations are limited, the overall average composition of oxide inclusions is not very different from that calculated at high temperature, as the amount of inclusions formed during the later stages is very small, for Al-killed steels (4).

Some of these oxide inclusions will serve as nuclei for the precipitation of MnS-rich inclusions during metal solidification. When CaO-rich oxide inclusions are thus entrapped in a manganese sulphide precipitate, further reaction can take place within the solidified metal, according to:



The final composition of the oxide and sulphide phases will depend on the relative amounts of oxygen and sulphur in the composite inclusion. The calculation of equilibrium composi-

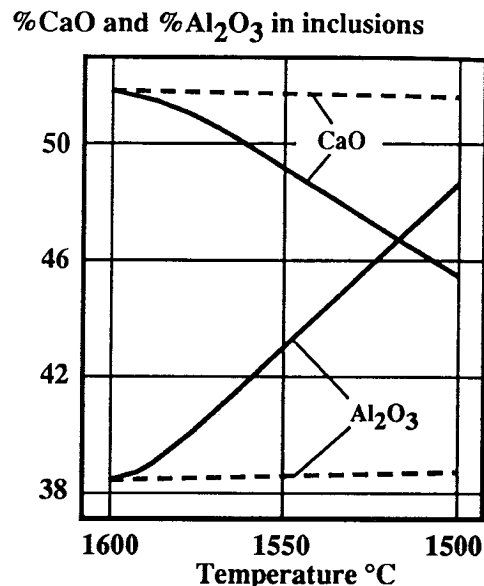
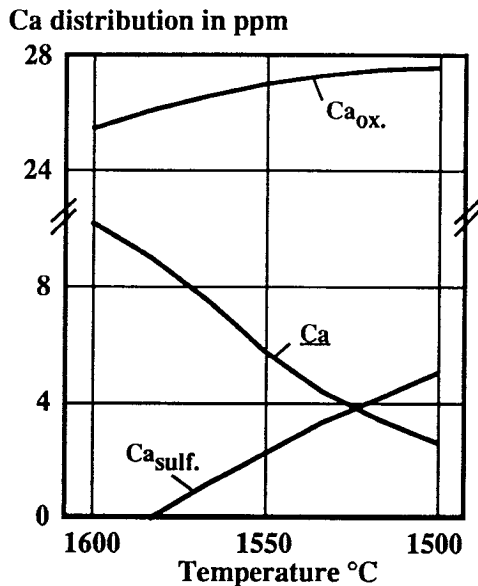


Figure 3: Computed precipitation path of inclusions in a Ca-treated 38CD4 steel (Ca treatment at 1600°C).
 ——— Composition of inclusions precipitated at the given temperature
 - - - - - Average composition of the oxide inclusions
 Steel composition: 0.015 %Al - 0.38 %C - 0.75 %Mn - 0.02 %S - 0.25 %Si - 35 ppm Ca - 30 ppm O
 Average composition of oxides: 9.4 %SiO₂ - 38.8 %Al₂O₃ - 51.6 %CaO - 0.1 %MnO

tion of the two phases calls for an accurate knowledge of the thermodynamic properties of both oxide and sulphide. If appropriate estimates are available for oxides, as shown in the previous chapter, this is not the case for MnS - CaS solid solutions.

III-1. Activity of CaS in the CaS - MnS solid solutions.

A laboratory study has been conducted in order to measure the activity of CaS in the MnS-rich corner of the CaS - MnS system (9).

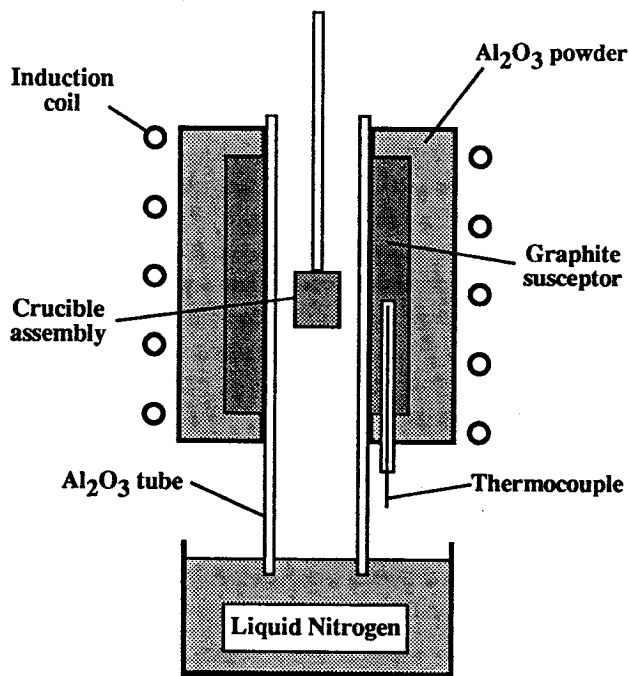
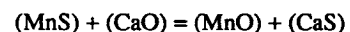


Figure 4: Sketch of the experimental apparatus used for the study of the CaS - MnS solid solution.

The experiments consisted in heating mixtures of MnS and Ca-aluminates (CaO/Al₂O₃ around 1) powders (a few grams) in iron crucibles. Several trials were made with variable respective amounts of MnS and Ca-aluminates. The experimental arrangement is shown in Figure 4. The samples were held for one hour at 1470°C, a time sufficient to obtain equilibrium, and then quenched in liquid nitrogen in order to maintain the high temperature compositions. The temperature of 1470°C was selected, as it is above the liquidus temperature of the oxides and below the solidus temperature of the crucible.

Figure 5 shows a section of the crucible after reaction. There is a clear separation of the two phases, the sulphide surrounding the oxide, as is observed for inclusions in steel. The composition of both phases was determined by microprobe analysis: there is a transfer of Ca from the oxide to the sulphide and the sulphide phase also contained small amounts of FeS (mole fraction of FeS below 0.3).

The value of the equilibrium constant for reaction



was determined from the thermodynamic data on the stability of the various compounds as reported in (10). At 1470°C, a

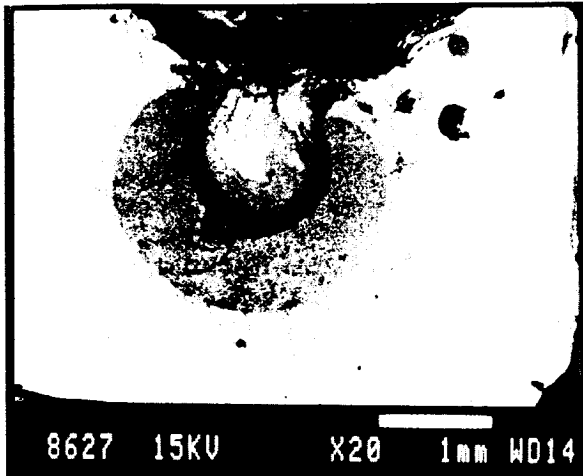


Figure 5: Global aspect of an iron crucible after reaction.
 dark grey: oxide phase.
 light grey: sulphide phase.
 white: iron crucible.

value of 0.67 is obtained for

$$K = (a_{\text{MnS}} \cdot a_{\text{CaO}}) / (a_{\text{CaS}} \cdot a_{\text{MnO}})$$

Thus, at 1470°C,

$$(\gamma_{\text{MnS}} \cdot N_{\text{MnS}}) / (\gamma_{\text{CaS}} \cdot N_{\text{CaS}}) = 0.67 a_{\text{MnO}} / a_{\text{CaO}}$$

The activities of oxide components were deduced from the analysis of the oxide phase, using the slag model. The resulting values of the ratio $\gamma_{\text{MnS}} / \gamma_{\text{CaS}}$ as a function of the composition of the sulphide phase are listed in Table I.

Table I: Ratio of MnS to CaS activity coefficient as a function of sulphide composition.

N_{MnS}	N_{CaS}	N_{FeS}	$\ln(\gamma_{\text{MnS}}/\gamma_{\text{CaS}})$
0.70	0.14	0.16	-0.48
0.61	0.16	0.23	-1.06
0.75	0.11	0.14	-0.52
0.73	0.20	0.07	-0.39
0.74	0.19	0.07	-0.80
0.70	0.13	0.17	-0.20
0.80	0.14	0.06	-0.50
0.69	0.03	0.28	-1.93
0.63	0.09	0.28	-0.91

When these results are analysed assuming that the thermodynamic properties of the MnS-CaS-FeS ternary system can be described using a Darken formalism (11), the following correlation is obtained:

$$\ln(\gamma_{\text{MnS}}/\gamma_{\text{CaS}}) = 0.84 + 3.49 N_{\text{CaS}} + 2.32 N_{\text{FeS}}$$

The activity coefficient of CaS at infinite dilution of CaS in pure MnS ($\gamma_{\text{MnS}} = 1$) takes a value:

$$\gamma_{\text{CaS}}^0 = 2.3 \text{ at } 1470^\circ\text{C},$$

indicating a positive deviation of the activity of CaS in the MnS - CaS solid solution.

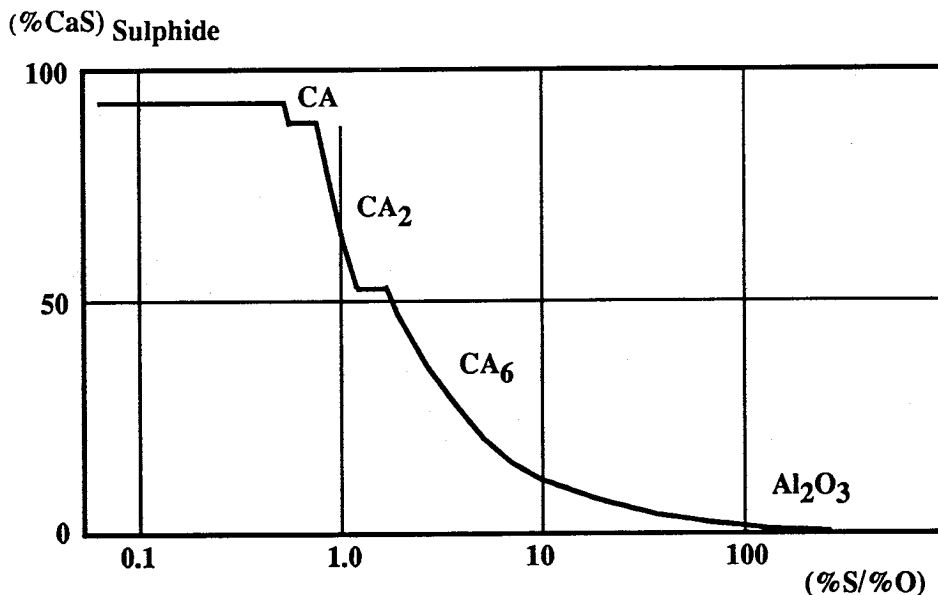


Figure 6: Influence of the ratio (%S/%O) in the composite inclusion on the nature of the oxide and on the CaS content of the sulphide after reaction.

III-2. Composition of the oxide / sulphide inclusions at equilibrium.

A model has been established to compute the equilibrium composition of the oxide/sulphide composite inclusion in the steel matrix (9). It takes into consideration:

- the composition of the Ca-aluminate formed in liquid steel during the calcium treatment,
- the relative amounts of oxygen and sulphur in the composite inclusion,
- the composition of the steel matrix.

As an example, Figure 6 describes the transformation of a composite inclusion having initially a core of Ca-aluminate of composition $\text{CaO-Al}_2\text{O}_3$. This figure shows, under the condition of equilibrium at 1470°C , the resulting composition of the oxide phase, and the CaS content of the sulphide phase, as a function of the ratio ($\%S/\%O$) in the composite inclusion.

For Al-killed Ca-treated steel grades well desulphurized, for which the global sulphur content is in the same range or smaller than the oxygen content, the composition of the oxide would be barely modified, but the CaS content of the sulphide phase would be very high.

For resulphurized free machining steels, on the contrary, for which ($\%S/\%O$) > 10, there is a strong possibility that the aluminates initially present in the liquid metal will be strongly depleted in Ca and will be transformed into globular nodules of $\text{CaO-6Al}_2\text{O}_3$ or even into pure alumina, whereas the CaS content of the sulphide phase will largely depend on the exact

amount of manganese sulphide precipitated around the oxide.

This mechanism has been confirmed by numerous observations of inclusions found in Ca-treated resulphurized steels. An example is shown in Figure 7, and similar observations have been made on numerous heats of the same grade (12). For this heat, the residual calcium content was around 20 ppm, with a total oxygen content in the same range. The composition of the oxide inclusions formed during the Ca-treatment was therefore around the stoichiometry of $\text{CaO-Al}_2\text{O}_3$. In solid metal, however, after precipitation of the sulphides, the X-ray images of the composite inclusions show that most of the calcium is present in the sulphide phase (Figure 5). A quantitative microprobe analysis of these inclusions shows that up to 90% of the total calcium of the examined sample may be present in the sulphide phase. This result shows, in particular, that for these steel grades, it will be difficult to control precisely the composition of the oxide inclusions and of the sulphides precipitated around them.

IV - RHEOLOGY OF THE OXIDE INCLUSIONS.

For some shaping operations such as thin wire drawing it is important that the residual fatal inclusions have undergone a drastic elongation during hot rolling operations. Similarly, for free machining steels, the desirable inclusions should have an appropriate plasticity at cutting temperature, in order to avoid abrasion of the tool and participate in the formation of a protective layer on the cutting edge. Inclusion morphology can also influence the mechanical properties and affect the surface aspect of finished products.

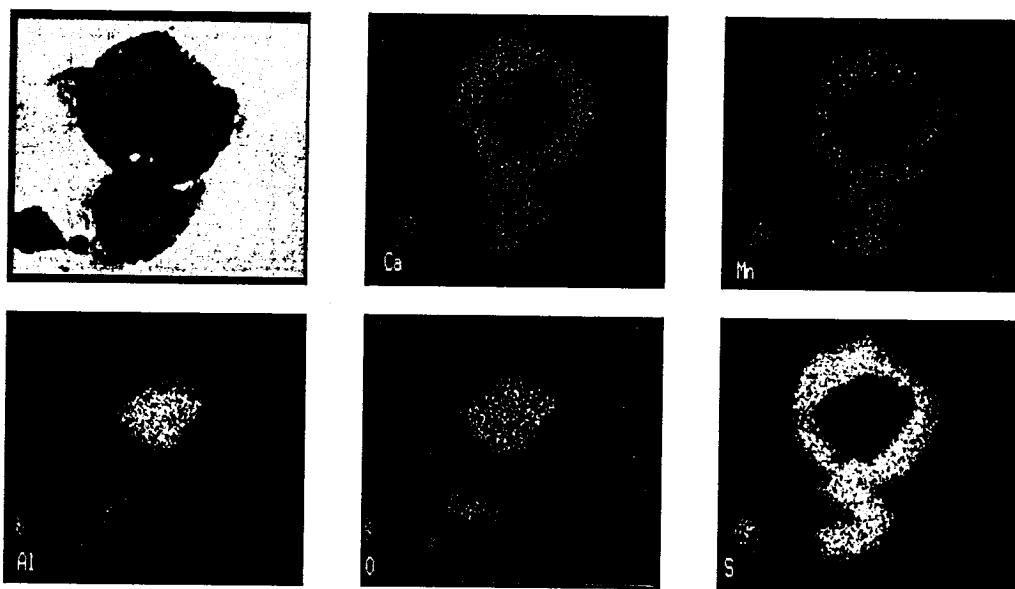


Figure 7: Repartition of elements (X-ray images) between oxide and sulphide phase of a composite inclusion in a resulphurized Ca-treated steel.

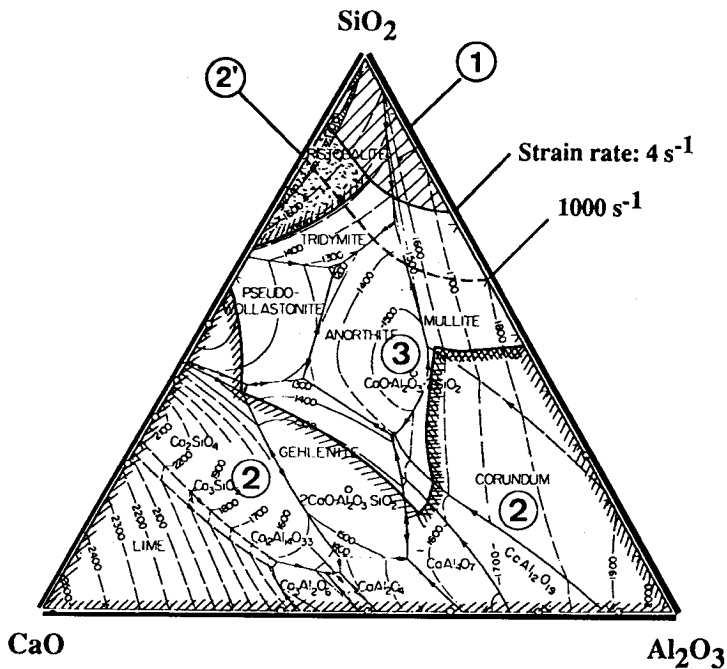


Figure 8: Limits of acceptable compositions of oxide inclusions for adequate deformation during hot rolling (after 7).

The important parameter governing the behaviour of inclusions during hot rolling is their relative plasticity with respect to that of steel under the corresponding conditions of deformation (temperature, strain, strain rate). A detailed discussion of these phenomena is proposed in Reference (7):

- glassy inclusion will either be easily elongated, if their viscosity is lower than the apparent viscosity of steel under the deformation conditions, or remain unaffected if their viscosity is higher. Inclusions consisting of two glassy phases (metastable miscibility gap in the silica rich domain) will behave in a similar manner: they remain undeformed if the viscosity of the more viscous phase is too high;

- crystallized oxide inclusions, either massive or in clusters, cannot be deformed during hot rolling. In some cases, they may be broken-up and leave an array of small crystallites oriented in the direction of deformation that can be observed on sections of the product;

- partially crystallized inclusions will be deformed if the viscosity of the liquid phase is lower than that of steel, but the individual crystallites will remain unaffected. Their degree of harmfulness will essentially depend on the proportion of crystallized phase.

Plasticity characteristics are available for some solid solutions of sulphides (13): the viscosity of CaS - MnS solid solutions increases sharply as the CaS content increases. Data is

Behaviour of inclusions during hot rolling of unalloyed steel (after 7).

- Rolling temperature: 1000°C.
- Strain: 0.1.
- Strain rate: 4 and 1000 s⁻¹, respectively.

1: Non deformable glassy inclusions: their viscosity is higher than that of steel for the conditions of deformation considered.

2: Non deformable inclusions: they are likely to be partially or totally crystallized in the as cast product. The heavy hatched limit corresponds to inclusions having a liquidus temperature higher than 1550°C and a viscosity lower than 10 Pa.s at liquidus temperature. The light hatched limit to inclusions having a liquidus temperature lower than 1550°C and a viscosity lower than 1 Pa.s at liquidus temperature.

2': Non deformable inclusions: they may be composed of two undercooled liquids, one of them having too high a viscosity.

3: Inclusions that are deformable for the deformation conditions considered, provided they have not recrystallized during the heating cycle prior to hot rolling.

also available for the main oxide systems, either from direct measurements or from extrapolation of viscosity data from higher temperatures. It has been found, in particular, that the high temperature viscosity measurements of silicates can be safely extrapolated to describe the behaviour of glassy inclusions at hot rolling temperatures. Analytical expressions as a function of composition and temperature are available (7).

On the basis of these considerations, diagrams such as the one presented in Figure 8 for CaO - SiO₂ - Al₂O₃ inclusions can be proposed. This diagram is based on the state of inclusions in the as-cast product and delimits the composition domain of inclusions that would remain glassy and have the appropriate viscosity requirements for adequate deformation. During the stay in reheating furnaces prior to hot rolling, however, some of the originally glassy oxide inclusions may recrystallize and thus become harmful. For instance, ruptures of steelcord attributed to recrystallized anorthite inclusions have been observed. Depending on the thermal history before hot rolling, it may therefore be desirable to restrict the inclusions within a narrower composition domain than shown on this diagram.

A laboratory study has been undertaken in order to get a clear understanding of the conditions of recrystallisation as a function of thermal history and oxides composition. Synthetic slags are melted in small iron crucibles and then rapidly cooled and held at given temperatures for various times. The time at which the first crystals appear is determined by obser-

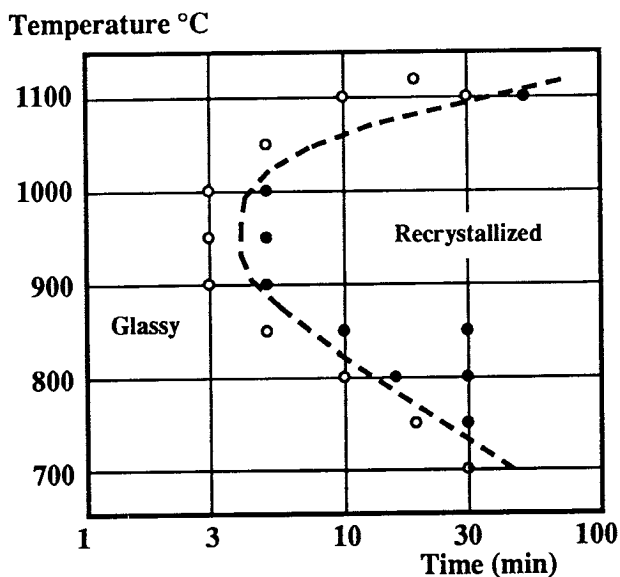


Figure 9: Recrystallisation TTT curve for an oxide mixture of composition 46.9 %MnO - 38.7 %SiO₂ - 10.1 %Al₂O₃.

vation of polished sections of the samples, and their amount can be determined either by image analysis or by X-ray diffraction. As an example, Figure 9 summarizes results for a composition of the MnO - SiO₂ - Al₂O₃ system located in the domain of Spessartite. Other experiments have been made for compositions in the CaO - SiO₂ - Al₂O₃ system with low liquidus temperatures (Anorthite, Pseudowollastonite and Gehlenite fields). They show that, for these low melting slags, the higher recrystallization rates are obtained for temperatures between 900 and 1200°C, which is precisely the domain of hot transformation for most steel products.

V - CONCLUSIONS

Various studies aimed at describing the behaviour of oxide and sulphide inclusions during secondary steelmaking treatments on liquid steel and their transformation in the solidified metal have been made.

The composition of endogeneous inclusions formed during the deoxidation treatment can be adequately predicted with a specific multiphase equilibrium calculation based on IRSID' slag model. Reliable results have been obtained for various deoxidation conditions (calcium treatment of Al-killed steels, Si-Mn deoxidation, ...) and for various steel grades (carbon steels or stainless steels). The model can be used to define optimal treatment conditions (e.g. slag monitoring of inclusions for ultra-low Al contents), to evaluate contaminations arising from late reoxidations, and as a control of steel quality from its global composition.

Important transformations that may affect the quality of the product can also take place during steel solidification (Ca transfer between Ca - alumino silicate inclusions and manganese sulphides that have precipitated around them), as well as during its transit in the reheating furnaces prior to hot rolling (recrystallisation of glassy oxide inclusions). An experimental study of the CaS - MnS solid solution has been made, and its results have been used to evaluate the extent of Ca transfer in composite oxide / sulphide inclusions. An experimental study of oxide inclusions recrystallisation shows that, for several compositions with low liquidus temperature, a maximum rate is observed in the 900 - 1200°C temperature range.

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