

SLAG MODELLING AND INDUSTRIAL APPLICATIONS

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Abstract

A bibliographical review of the most recent developments in slag modelling approaches, published since the 5th International Conference on Molten Slags, Fluxes and Salts, is presented, and the trends in using this information in Computational Thermodynamics software/database packages are outlined.

Industrial applications based on examples pertaining to various Iron- and Steelmaking reactors are discussed. These applications made essentially with the IRSID slag model and the CEQCSI software concern metal refining or micro alloying by slag-metal reactions and inclusions control in steels.

Introduction

Models for the estimation of the thermodynamic properties of metallurgical slags and fluxes find their natural expression in Computational Thermodynamics software/database packages which have been developed in the last two decades. The most widely used commercially available packages, Thermo-Calc [1], FACT [2], ChemSage [3], MTDATA [4] and GEMINI2 [5] combine computation codes for multiphase, multicomponent equilibria calculation and databases and have found extensive applications in the metallurgical, materials and chemical engineering industries.

At IRSID, a non-commercially available package called CEQCSI [6], based in a large part on the IRSID slag model, has been developed for very specific applications in the field of Iron and Steelmaking. It is well adapted to the following situations :

- calculation of slag crystallisation path in order to determine, for instance, the evolution of its liquid fraction as a function of temperature,
- calculation of slag-metal equilibrium in order to determine, for instance, the transfer from the slag to the metal of trace elements Ca, Mg, and in some grades Al, at the level of a few ppm to fractions of ppm, that may influence the nature of inclusions present in the product,
- calculation of inclusions precipitation in order to determine, from the overall steel analysis, the amount, composition and origin (ladle treatment, steel cooling and solidification, solid metal) of endogeneous inclusions and precipitates.

This paper will review the developments, published since the 5th International Conference on Molten Slags, Fluxes and Salts, concerning experimental determinations of slag thermodynamic properties, progress in slag modelling, and will outline the trends in using this information in Computational Thermodynamics packages. Some industrial examples based essentially on the IRSID experience in Iron and Steelmaking applications will then be presented.

Experimental data and slag modelling

Recent experimental studies of slag thermodynamic properties

Although an exhaustive review of phase diagrams studies is out of the scope of this paper, a few studies are reported here, as they were designed for expanding the database for the FACT system. They concern systems containing PbO and ZnO [7-8], and the effect of MgO and Al₂O₃ on the liquidus temperatures of the fayalite field in the Al₂O₃-MgO-“FeO”-CaO-SiO₂ system in equilibrium with metallic iron [9-10]. A study concerning the Al₂O₃-CaF₂-SiO₂ system [11] of direct interest for steelmaking was also reported.

Activities determinations for oxide components in slag systems have shown a sustained interest, with maybe an approach less systematic and more oriented towards previously unexplored domains than in the past decade. They concern, in particular, measurements of FeO activities in steemaking ladle slags with low FeO content [12-17, 20] or BOF slags [24], MnO activity in BOF [18,24] and ladle slags [19-20], P_2O_5 activities in various steemaking slag systems [24-27], Cu, Pb and minor elements solubility in Iron-silicate slags [22-23]. A rather large number of studies concern slag systems containing Cr oxides [28-31] or Ti oxides [22-36].

Sulphide capacities have been the object of several studies [37-43] with, in particular, a very thorough investigation of subsystems of the “FeO”- Al_2O_3 -CaO-MgO-MnO-SiO₂ system by Seetharaman et al. at the Royal Institute of Technology in Stockholm.

Special mention has to be made of the studies performed by Suito et al. at Tohoku University. They have concluded a long list of investigations of slag activities measurements presented in the last decade by an exhaustive study of activities of SiO₂ and Al_2O_3 , activity coefficients of FeO and MnO, and MgO saturation in the CaO-SiO₂- Al_2O_3 -MgO system [20]. In addition, their very elegant studies on deoxidation equilibria in liquid iron [44-46] provide a very convincing explanation to a long unresolved apparent discrepancy between solubility products of CaO (MgO) obtained from liquid phase measurements and thermodynamic estimations at infinite dilution in Ca (Mg) and O. Indeed, several regions are observed for the value of apparent solubility product as the content in (%Ca + 2.51 %O) is increased, with first a very sharp increase for low values of this parameter, and a levelling off at higher values. They proposed coherent sets of first and second order interaction coefficients between Ca and O and between Mg and O (different values for the different composition domains) to explain satisfactorily the measured solubilities of CaO and MgO.

Hino et al. [47], who had previously been intense providers of new experimental data including data estimated from Gibbs-Duhem integration or models, intend to orient their studies to a direct measurement of all component activities in selected domains where actual data seem uncertain (for instance, the low SiO₂ domain in the CaO- Al_2O_3 -SiO₂ system). To that effect, they have performed mass-spectrometry activity measurements of the constituents in liquid Cu-Al, Cu-Mg, and Cu-Ca alloys that will be used as equilibration media.

Recent developments in slag modelling

A good deal of efforts have been devoted to expanding the databases covered by existing models, with maybe fewer propositions of new models than in previous periods.

Thus, the database for the FACT system has been largely increased by critical assessment of various binary, ternary and quaternary oxide systems [48-50], using the modified quasichemical model for the slag phase. In addition, the same modified quasichemical model

for short range ordering was used for the thermodynamic modelling of liquid Fe-Ni-Cu-Co-S [51] and Co-Fe-Ni-S [52] mattes, leading to the construction of a complete database for copper smelting and refining [53]. This database was subsequently extended for calculations in the Zn-Pb-Cu-Ca-Fe-Si-O-S system [77-78]. In this database, the slag, matte and alloy phases are treated as different phases, all described by the modified quasichemical model, and the sulphide solubility in the slag is predicted by the Reddy-Blander model, as modified by Pelton. The modelling of matte and slag as one oxysulphide phase is announced as being the subject of future work.

One of the important developments of the Thermo-Calc database is the assessment of the Ca-Fe-O-Si system [54-55]. In this assessment, both liquid metal and CaO-FeO-Fe₂O₃-SiO₂ slag system are described with the ionic two-sublattice model, with a single set of parameters. Another development at the KTH concerns the use of a previously proposed model [56] for the description of the measured sulphide capacities in multicomponent slag systems. In this model, the slag composition is described using a modified Temkin approach, where complex polymeric ions are considered as dissociated to simple species. It has been applied for predictions of sulphide capacities in the "FeO"-Al₂O₃-CaO-MgO-MnO-SiO₂ slags [42]. A new mathematical model has also been developed to predict the thermodynamic properties of the liquid phase in multicomponent slag systems using only information from the binary subsystems [57]. It uses Temkin's description of the entropy of ionic melts coupled with Lumsden's description of silicate and aluminate melts, where the ionic melts are considered as an oxygen-ion matrix with the cations distributed in it. It has been applied to compositions in the Al₂O₃-CaO-MgO-MnO-SiO₂ with a generally satisfactory agreement with experimental values, and also some disagreements which are judged as being indicative of the need for further reliable experimental information.

At IRSID, the cell model for oxides and diluted sulphur was applied to describe the behaviour of Ti oxides in multicomponent slags [58]. It is presently used for calculations in the system SiO₂-TiO₂-Ti₂O₃-Cr₂O₃-Al₂O₃-Fe₂O₃-CrO-FeO-MgO-MnO-CaO-CaF₂-S. The oxy-sulphide model [59] has also been consolidated for the system SiO₂-Al₂O₃-Fe₂O₃-FeO-MgO-MnO-CaO-S. In these cell models, the multicomponent systems are described using only binary parameters.

Mogutnov et al. [60] have developed an associated-solution model of liquid slags and silicates, based on Prigogine's theory, and have applied it with success to ternary and quaternary compositions of the CaF₂-CaO-Al₂O₃-SiO₂-MnO-Ca₃P₂ system.

The Lin and Pelton [61] structural model has recently been reactivated and extended by Serrano and Pelton [62] to the ternary systems SiO₂-MnO-MgO, SiO₂-FeO-MnO and SiO₂-FeO-MgO. The authors state that further studies are needed to complete the model in order to take into account more complex silicates such as SiO₂-FeO-CaO where the behaviour of Fe²⁺

and Ca^{2+} is very different in the silicate structure, and a random mixing can no longer be assumed. They also mention that this structural model can be used to predict sulphide capacities of the melts, since S^{2-} can be easily incorporated into one self-consistent model, substituting on quasi-lattice sites for O^{2-} . The same model has also been applied for alkaline binary and ternary silicates [63].

Another novel approach is the use of molecular dynamics simulations, which had in the past been applied to various refining slags [64], to describe the behaviour of diluted oxides and fluorides in the CaO-CaF_2 system [65]. The future developments of this method for complex systems is quite uncertain.

Very little has been recently published concerning the use of optical basicity in slag modelling and process control. A user friendly software package has however been developed, with the purpose of providing an access to the Optical Basicity Databank for technological applications and for the purposes of scientific evaluation [66].

An interesting comparative study of various models has been made for MnO- containing slags relevant to ferromanganese melting [67]. In this study, the UIPM (unified interaction parameter model), regular solution model, associated solution model, two-sublattice model, polymerisation model, modified quasichemical model and cell model were considered, and their applicability to metal and slag phases was assessed. The final choice was to select the UIPM model for the metal phase, and the cell model for the slag phase, with however revised values of the parameters originally proposed at IRSID for a better fit in the composition domain concerned.

Trends in Computational Thermodynamics.

A recent update of the current status of the main commercial computational thermodynamics packages has been presented at the last IUPAC Conference (Jülich, April 2000).

A strong trend is increased cross-breeding of the contributions of the various teams. Developments in data assessments and solution models had previously been widely shared on a scientific basis (for instance, assessments provided by the Thermo-Calc and FACT groups had found a very large audience in the scientific community, early versions of the IRSID slag model were available in the databases of Thermo-Calc and ChemSage, ...); some software products are now developed in common by some of the teams. It has thus been announced [68] that the FACT and ChemSage groups were proposing common packages called FACTSage and ChemApp with enlarged database platforms and improved users friendly access.

Another trend is the increased coupling of purely thermodynamic packages with kinetic models. For instance, the coupling of Thermo-Calc and DICTRA [69] provides a unique commercial software which can precisely simulate diffusion-controlled phase transformations in various materials. DICTRA uses Thermo-Calc as its engine for thermodynamic calculations, but extends to applications with kinetic problems engaged.

Several industrial applications involving the coupling of CFD codes and thermodynamic models have been proposed. For instance, a new modelling approach has been put forward to study slag-metal reactions, applied to sulphur refining in a gas-stirred ladle [70]. A two-dimensional fluid dynamic model accounting for the steel, slag and argon phases has been incorporated with the thermodynamics model of desulphurisation developed at the KTH. Comparison of the model calculations with plant data from Ovako Steel indicates that this approach has great potential. Another application [71-72] concerns the coupling of a CFD code of the steel ladle and thermochemical softwares (MTDATA and ChemSage) in order to understand the individual mechanisms that take place during inclusion generation, their interaction with steel, refractories, slag and atmosphere, and their removal from or retention in the steel. The aim of this study is to assess the relative importance of all inclusion sources and help steelmakers define process routes for optimum steel cleanliness. A similar approach involving the coupling of CEQCSI with a CFD code had been developed to study mass transfer and inclusions precipitation during the elaboration of Nickel alloys in a vacuum induction furnace [73]. The aim, in particular, was to study the result of calcium treatments involving strong interactions with the MgO lining. Other applications concern the coupling of CEQCSI with a nucleation and growth model to study the kinetics of inclusions precipitation during steel solidification [74], and a very ambitious, albeit somewhat simplistic approach, using ChemSage for the simulation of an LD-converter process [75-76].

Industrial applications : slag-metal reactions

One of the more obvious uses of Computational Thermodynamics packages in extractive metallurgy is the evaluation of the equilibrium distribution of elements between various phases, and the definition of appropriate conditions for optimal metal purification.

A very significant example is the application of the F*A*C*T thermodynamic computing system for the thermodynamic modelling of lead and zinc distribution among matte, slag, liquid copper and gas phases during copper smelting and converting [77-78]. This required calculations in the 8-component system Zn-Pb-Cu-Ca-Fe-Si-O-S. Model evaluations were compared with available experimental data, and predictions have been proposed in situations where experimental data are difficult to obtain.

In the field of steelmaking, a very detailed analysis of ladle steel desulphurisation on thermodynamics grounds has recently been made [79-80]. The authors tested different models to express the slag sulphide capacity, and evaluate the oxygen activity at the slag metal interface from the Al/Al₂O₃ equilibrium, and found that the best agreement between calculated and analysed sulphur distributions is obtained by combining the KTH model for sulphide capacity [40], and the expression of Al₂O₃ activity recently proposed by Ohta and Suito [20].

This example is a very convincing demonstration of the usefulness of industrial data to confirm thermodynamic estimations. Some care has however to be taken in order to eliminate a possible bias than can occur from kinetic limitations :

- whenever possible, a cross-check of different means to evaluate a given quantity should be combined. For example, Figure 1 indicates results of successive samples taken during a slag-metal stirring treatment under vacuum [81]. The oxygen activities at the slag-metal interface evaluated for the Si/SiO₂ and Mn/MnO are in relative good agreement for all samples, whereas the activity evaluated from the Al/Al₂O₃ equilibrium is much lower in the first sample and progressively comes to agreement with the other estimations. Indeed, sample 1 was taken rather early after a late Al addition to the metal, and complete oxidation of the excess Al took some time (more than was realised in standard practice). Note that in this case, the oxygen activity does not level-off as a sign equilibrium is reached, because the temperature was constantly decreasing. Note also that oxygen activities measured in the metal are by no means representative of the activities at the interface. Indeed, oxygen in the metal is usually buffered by the strongest deoxidising element and its pure oxide (in general Al/Al₂O₃), as there is a constant intake from the refractories, and even locally from the probe itself. The measured value is thus bound to be higher than the value at the interface.

- whenever possible, an estimation of time required to reach equilibrium should be made. Figure 2 summarises a thorough analysis of ladle steel desulphurisation [82] in terms of thermodynamic factor (λ , product of equilibrium sulphur distribution ratio and slag relative consumption) and kinetic factor (B, product of mass transfer coefficient, cross section to metal volume ratio and time). On this diagram, equilibrium is reached on the horizontal asymptote of the constant desulphurisation ratio curves. An interesting result is that, for given stirring conditions, the time necessary to approach equilibrium within a given percentage increases with S equilibrium distribution ratio.

Besides metal refining, slag metal treatments can be used for accurate and smooth micro-alloying of the metal, in conditions that will prevent artefacts arising from local supersaturations when the alloying element comes in contact with the metal. Such treatments in the case of Ti transfer from slag to metal have been recently analysed at IRSID [83]. The trials were made under stirring conditions expected to reach equilibrium in the same vacuum ladle equipment as in [81] and concern Al-killed stainless steel grades containing 0.1 to 4 %Ti

and semi-killed stainless steel grades with lower Ti contents ($Ti < 0.003\%$). The range of basic slags used during the elaboration of the first grade is wide : TiO_2 up to 26%, SiO_2 from 0 to 8%, Al_2O_3 from 20 to 30%, CaO from 30 to 60% and MgO from 3 to 20%. The range of temperature is also wide : between 1475°C and 1630°C. For the second grade, the slags have lower contents in titanium oxides ($TiO_2 < 1\%$) and higher silica contents (SiO_2 from 13 to 35%). A few carbon steels were also studied. Figure 3 compares the oxygen activities calculated from the Ti/TiO_2 (taking into account Ti^{3+} and Ti^{4+}) and either Al/Al_2O_3 or Si/SiO_2 equilibria (and in some cases both). A general agreement is observed, confirming the validity of thermodynamic estimations.

The titanium equilibrium distribution ratio between reduced ladle metallurgy slags and steel depends essentially on the oxygen potential, that is on metal Al content. A variation of $\%CaO / \%Al_2O_3$ has relatively little effect on the distribution ratio, whereas an increase in the TiO_2 content or temperature induces an increase in calculated equilibrium distribution ratio. This is illustrated on figure 4 which combines data for carbon and stainless steels. On this diagram :

- the titanium oxide content of the slag is expressed as $\% TiO_2$, although the calculation takes into account Ti^{3+} and Ti^{4+} ,
- the steel characteristics are expressed with the Ti and Al activities, to combine information on carbon and stainless steels. For carbon steels, the activities are practically equal to the contents in weight %, whereas they are substantially different in the case of stainless steels ($a_{Al} \sim 3$ to 4 times $\%Al$, and $a_{Ti} \sim 7$ to 8 times $\%Ti$ for the grades considered).

The lines represent model calculations for slag compositions 5% and 10% TiO_2 , 10% MgO , $\%CaO/\%Al_2O_3 = 1.4$ at 1500°C and 1600°C, and the experimental points represent industrial data for slag compositions somewhat scattered around these values.

Industrial applications : Metal-Refractories interactions

Laboratory experiments were made at IRSID [83] to study the effect of the reduction of MgO-based refractory by Al-Ti- deoxidised steels on the composition of oxide inclusions. Batches of 1 kg steel containing 0.12 %Mn and 0.03 %Si were melted in sintered MgO crucibles and held under purified argon at 1580°C for times of 20 minutes to 1 hour in an air-tight induction furnace. Metal samples were taken every two to five minutes by suction in silica tubes and rapidly cooled. The samples were then analysed, and observations and micro analysis of inclusions were performed. The observed inclusions have a diameter of one to a few microns and pre-existed in liquid metal, the inclusions formed during solidification of the samples being much smaller. They are much more abundant in the first samples than in the samples taken later-on.

The evolution of steel composition and nature of inclusions depend on Al and Ti initial contents. For two extreme cases, the results are as follows :

- for an initial composition 0.03% Al, 0.04% Ti, there is first a continuous decrease in Al only, and the Ti content starts decreasing only when the Al content reaches about 0.006%. The inclusions consist of a mixture of alumina inclusions and spinels, the proportion of spinel increasing with reaction time.

- for an initial composition 0.006% Al, 0.08% Ti, both Al and Ti contents decrease all along the experiment. Two types of inclusions were observed : spinels and a phase rich in Al_2O_3 and TiO_2 .

In both cases, there is an increase in metal Si content, and a very slight increase in Mg content, this magnesium being concentrated in the spinel inclusions. Mass balances indicate that most of the reoxidation can be attributed to the reduction of SiO_2 from the crucible, a very small reoxidation arising also from the gas phase.

On Figure 5, we have plotted the evolution of metal composition, superimposed on the phase diagram for the system Fe-0.12 %Mn-0.03 %Si-Al-Ti-O at 1580°C, as calculated using the slag model. This diagram indicates the nature of the first oxides formed as a function of dissolved Al and Ti contents, and the values of the oxygen activities at equilibrium between these oxides and the metal. When traces of Mg are added to the metal, the calculation indicates that, upon reaching oxygen saturation, the first oxide formed is a spinel (Mg,Mn)O- Al_2O_3 which coexists with either Al_2O_3 or liquid oxides. The dotted line in Figure 5 indicates the limit between these two domains for 0.5 ppm Mg. When, for a given amount of oxygen in excess of saturation, the metal Al content decreases, in the domain of liquid oxides, more and more of the magnesium is fixed in the liquid oxides, so that the amount of spinel decreases, and can even disappear. In the stability domain of Al_2O_3 , on the contrary, the spinel phase will always be present.

The calculation with the CEQCSI software of inclusions amount and composition from the elementary analysis of the metal samples is summarised on Figure 6. It appears that the nature of equilibrium inclusions is in good agreement with the observations. In particular, the phase rich in Al_2O_3 and TiO_2 formed in the low aluminium grade is indeed issued from the liquid oxides that were present at 1580°C.

Industrial applications : Inclusions control in steels.

The procedure used in the CEQCSI software to calculate, from the overall elementary steel analysis, the sequence of precipitation of inclusions at equilibrium is applied by steps from the temperature of liquid steel treatment, to subsequent temperature evolution, during cooling and solidification of the steel. In this last situation, an original method has been

developed [84] in which the micro-segregation equations for elements dissolved in liquid metal, with or without diffusion in solid metal, and the equilibrium conditions between liquid steel and oxide, sulphide, nitride, or carbide precipitates are treated simultaneously. The calculation also gives the liquidus temperature of the oxide inclusions and their crystallisation path during cooling.

Various applications, in particular concerning semi-killed steels in which the formation of liquid oxide inclusions is required, have been discussed in detail [85]. The calculation, in agreement with extensive samples analyses, allows a discrimination of deoxidation inclusions which typically consist of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ with small amounts of MgO and MnO , and inclusions formed during solidification or arising from late reoxidations with compositions in the $\text{MnO-Al}_2\text{O}_3\text{-SiO}_2$ system. Defective treatments usually occur because the contents in tramp elements Al, Ca and Mg in liquid steel are too high, and applications of the CEQCSI software can be used to define a method of controlling the contents in these tramp elements by an appropriate slag-metal treatment in the ladle.

The examples presented here illustrate new facets opened by the latest developments of the IRSID slag model, in particular concerning Ti oxides and oxisulphides.

Calcium treatment of Al-killed steels.

Calcium additions are widely used in steelmaking to control the morphology of oxide inclusions and sulphide precipitates. In the present application (steel of composition 0.8 %C-0.65 %Mn-0.2 %Si-0.13 %Cr with Al contents varying between 150 and 650 ppm), the treatment is performed in order to transform alumina inclusions into liquid calcium aluminates, in order to prevent nozzle clogging during continuous casting. During the treatment, only a small part (about 15 to 20%) of added calcium remains in the metal, the rest being lost by vaporisation. The calcium remaining in the metal at treatment temperature consists of :

- Ca contained in oxide inclusions. If this amount is too small, solid aluminates are formed ($\text{CaO.6Al}_2\text{O}_3$, $\text{CaO.2Al}_2\text{O}_3$, $\text{CaO.Al}_2\text{O}_3$) which are even more detrimental than alumina inclusions with regard to nozzle clogging,
- Ca dissolved in liquid metal, this amount being larger at higher Al content. Most of this calcium will form precipitates of CaS or $(\text{Ca,Mn})\text{S}$ during steel solidification,
- possibly Ca contained in calcium sulphide in the liquid steel if the CaS saturation limit is reached. In this case, the CaS precipitates formed in liquid metal can also contribute to nozzle clogging, and the amount of residual calcium may be too small to form liquid aluminates.

Figures 7 and 8 summarise, for Al contents of 650 and 150 ppm, respectively, the calculated distribution of calcium among these various phases, as a function of total Ca and O contents fixed in the metal at the end of the calcium treatment. On these diagrams, the red

lines represent the limits of existence of the various oxides, that is, for increasing calcium content at a given oxygen content, solid aluminates in the domain labelled "Solid Oxides", mixture of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and liquid oxides (from 0 to 100 % liquid) in the domain labelled "CA + liq", and liquid oxides of increasing CaO content in the domain labelled "Liquid Oxides". The blue lines indexed with S contents indicate the calcium content for which calcium sulphide saturation is reached for the given S content. In the domains "CA + liq", the S content for CaS saturation is practically constant, 90 ppm S for 650 ppm Al and 450 ppm S for 150 ppm Al.

These diagrams indicate the windows available for a proper transformation of alumina inclusions into fully liquid aluminates without CaS precipitation in liquid steel. It is apparent that for the steel grade with 650 ppm Al, this window is completely closed for an S content as low as 90 ppm, whereas for the steel grade with 150 ppm Al, an adequate transformation of oxides can be obtained without CaS precipitation for much higher S contents.

Inclusions in Ti-deoxidised Steels

Towards the end of the 80's, NSC researchers, during the development of the so-called "Metallurgy of oxides in steels" [86-87], began to be interested in the precipitation of various inclusions during solidification of steel. It has been shown that inclusions containing both Al_2O_3 and TiO_2 formed during solidification of steels for tubes or plates, and on which manganese sulphides can precipitate, can serve as nucleation sites for acicular ferrite after welding or heat treatment.

The diagram of figure 9 is the computed equilibrium diagram for the system Fe-Ti-Al-O at 1520°C, that is at liquidus temperature for the considered steel grades. The small amount of dissolved oxygen will form the desirable inclusions during steel solidification. It is apparent from this diagram that very low Al contents (below about 40 to 50 ppm) have to be reached in order to obtain endogenous oxide inclusions containing titanium oxides in steels containing about 100 to 200 ppm Ti. In traditional Al-killed IF steels stabilised with Ti, the equilibrium deoxidation product is alumina; the Ti containing oxides commonly found in SEN deposits are presumably the result of reoxidations in the nozzle.

The calculated amounts of oxides formed at equilibrium during the solidification of such a steel grade, as a function of Al content, are indicated in figure 10. The oxide inclusions were originally liquid when formed, and a complete crystallisation has been assumed. The occurrence of these various phases has been verified in laboratory and industrial heats. The model has thus been used to define the optimal steel compositions in terms of Al and Ti contents to maximise the amount of oxide active particles, one of them being Al_2O_3 - TiO_2 phases : the desirable composition is Ti in the range 100 - 200 ppm and Al in the range 20 - 30 ppm.

Inclusions in free cutting steels.

In these steel grades with high S contents, two main objectives are sought :

- obtain a good distribution of MnS precipitates to limit the chips length,
- avoid the contact of the tool with hard abrasive oxides (Al_2O_3 , spinels ...) by avoiding their formation or embedding them in sulphides.

In addition, for high speed machining, it is favourable to harden some of the sulphides that will then form protective films on the tool. One way to do this is to add calcium to form $(\text{Ca},\text{Mn})\text{S}$, another way is to obtain oxisulphides in which the hardening effect is created by the partial substitution of S by O. This last solution is applied for free cutting steels.

Calculations were made to predict the nature of oxide, oxisulphide and sulphide phases precipitating in liquid steel and during solidification, in a base steel of composition 0.07 %C-1.35 %Mn-0.014 %Si containing minute amounts of tramp elements Al, Ca and Mg resulting from the ladle treatment, as a function of oxygen content (20 to 120 ppm). The calculated sequence of inclusions precipitation for an oxygen content of 60 ppm is indicated in Figures 11 (oxygen distribution in the various precipitates) and 12 (sulphur distribution in the various precipitates).

A summary of the effect of oxygen content on the amount of the various oxide, oxisulphide and sulphide phases is presented in Figures 13 and 14. It appears that the optimal oxygen content is around 60 ppm, as the amount of oxisulphides is large, and the amount of harmful oxides is minimised. This oxygen range has indeed shown the best free cutting properties in industrial casts.

Conclusions

Intensive efforts have been made in the last few years to use established slag models for the appropriate description of more and more complex systems, and incorporate them in Computational Thermodynamics software/database packages. It is expected that the use of these models and confrontation with industrial results will help in defining the specific domains in which further experimental investigations of slag thermodynamic properties are needed and avoid duplication of studies in domains in which the data is fairly well established.

At this time, it does not seem that purely new slag modelling concepts that would substantially change the picture in the next few years have come to age.

An ever increasing number of industrial applications in the fields of metallurgical, materials and chemical engineering industries, that take full advantage of the models and of

the accessibility of powerful calculation codes have been proposed and they generally show very encouraging results. More and more, the opportunity of coupling thermodynamic codes and CFD or kinetic codes is put into effect for a better understanding of processes and materials design.

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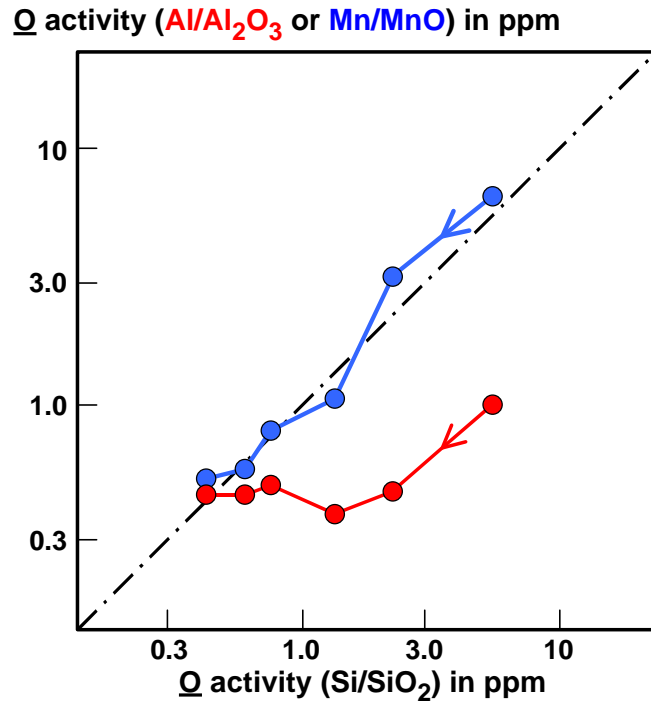


Figure 1 : Evolution of the oxygen activity calculated for the Si/SiO₂, Al/Al₂O₃ and Mn/MnO equilibria for six successive slag and metal samples taken during a ladle treatment under vacuum.

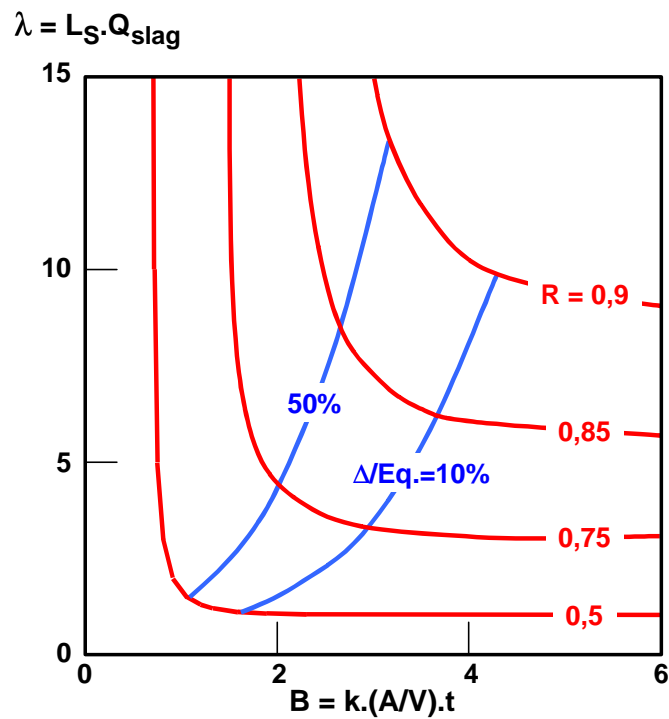


Figure 2 : Analysis of ladle steel desulphurisation in terms of thermodynamic parameter λ and kinetic parameter B . For given stirring conditions, the treatment time necessary to approach equilibrium within a given percentage increases with desulphurisation ratio R (i.e. with S equilibrium distribution ratio).

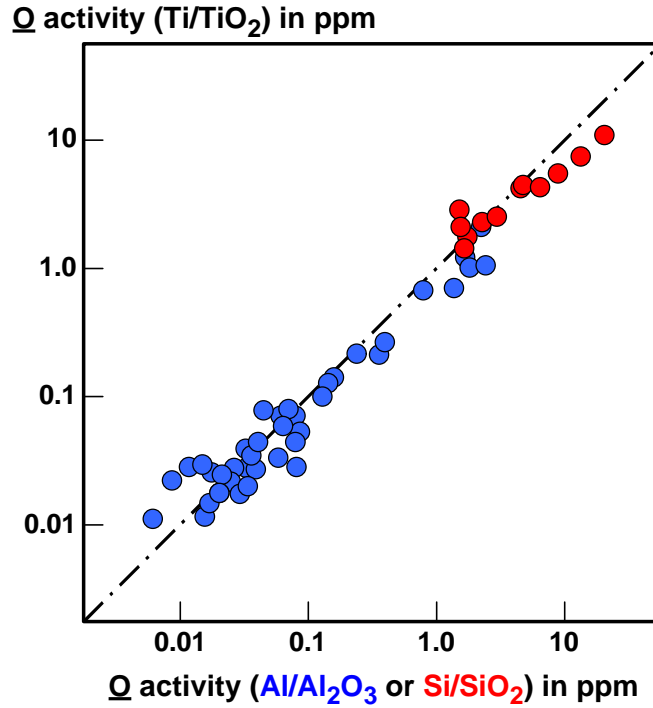


Figure 3 : Comparison of the oxygen activity calculated from the Ti/TiO₂ and either Al/Al₂O₃ or Si/SiO₂ equilibria for various ladle treatments under vacuum on carbon and stainless steels.

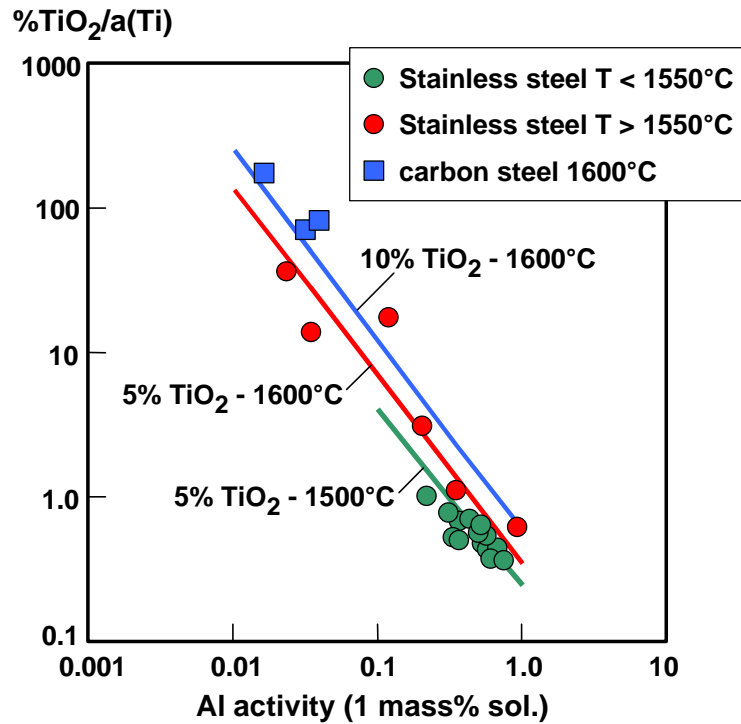


Figure 4 : Evolution of Ti equilibrium distribution ratio between slag and metal, as computed with the CEQCSI software, and comparison with industrial data of ladle treatments under vacuum on carbon and stainless steels.

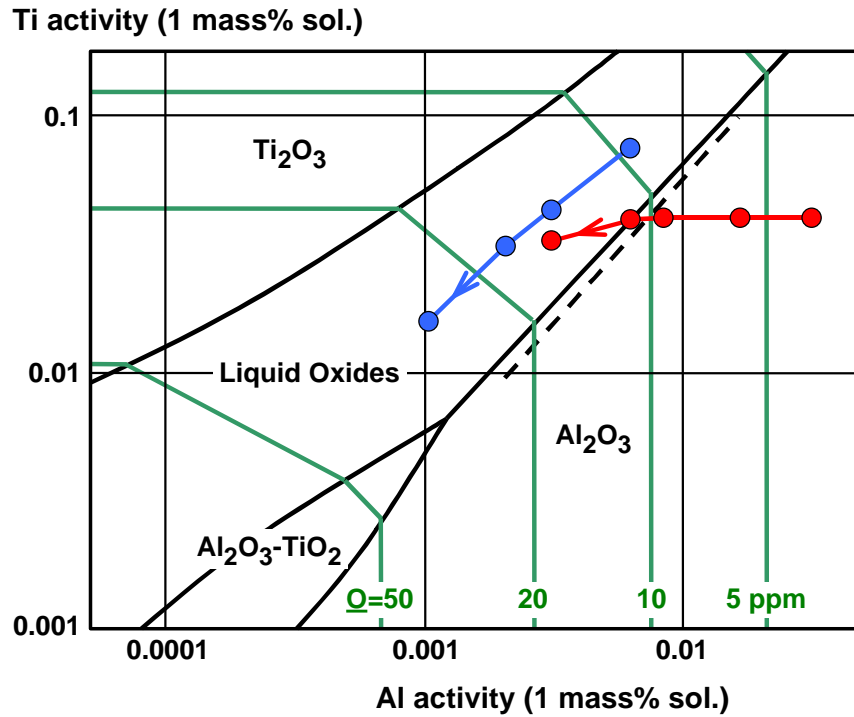


Figure 5 : Evolution of metal composition during two oxidation treatments in the laboratory, plotted on the computed equilibrium diagram for the system Fe-0.12%Mn-0.03%Si-Al-Ti-O at 1580°C.

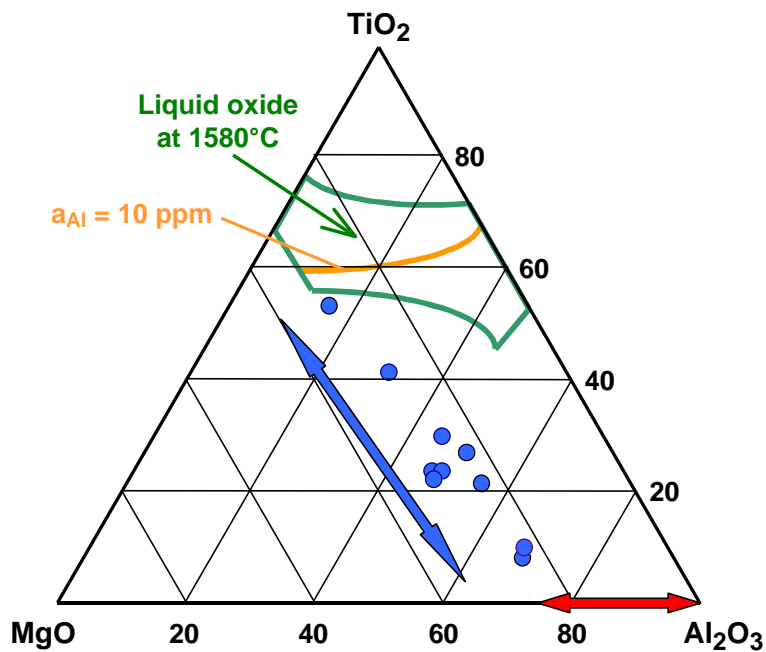


Figure 6 : Calculated (arrows) and observed (dots) composition of inclusions in various samples of the two steel grades studied. The red arrow corresponds to the trial with initially 0.03%Al, the blue arrow and dots to the trial with initially 0.006%Al.

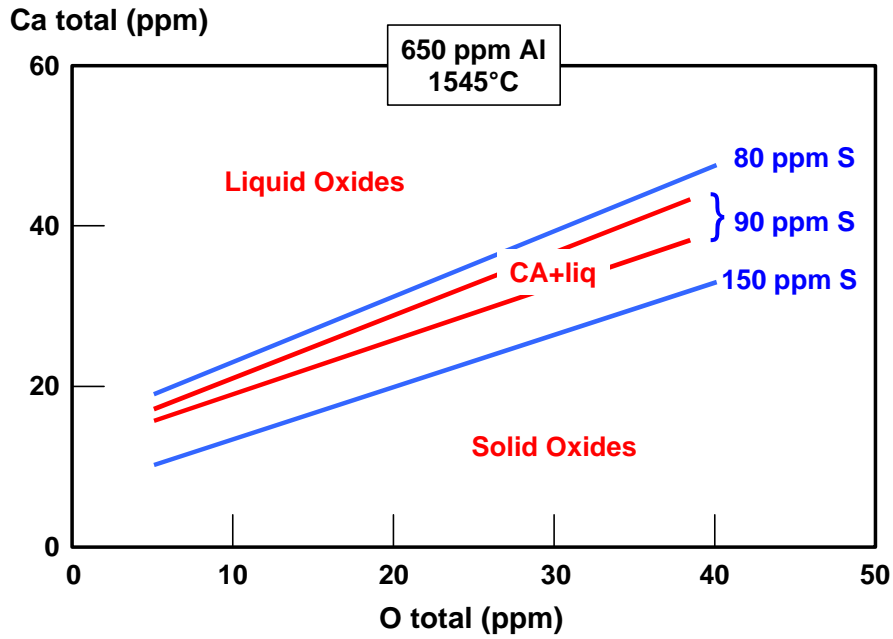


Figure 7 : Nature of oxide phases formed as a result of Ca treatment of a steel grade containing 650 ppm Al, as a function of Ca and O contents. The lines indexed with S content indicate the minimal value of Ca content leading to CaS precipitation in liquid steels, for the given S content.

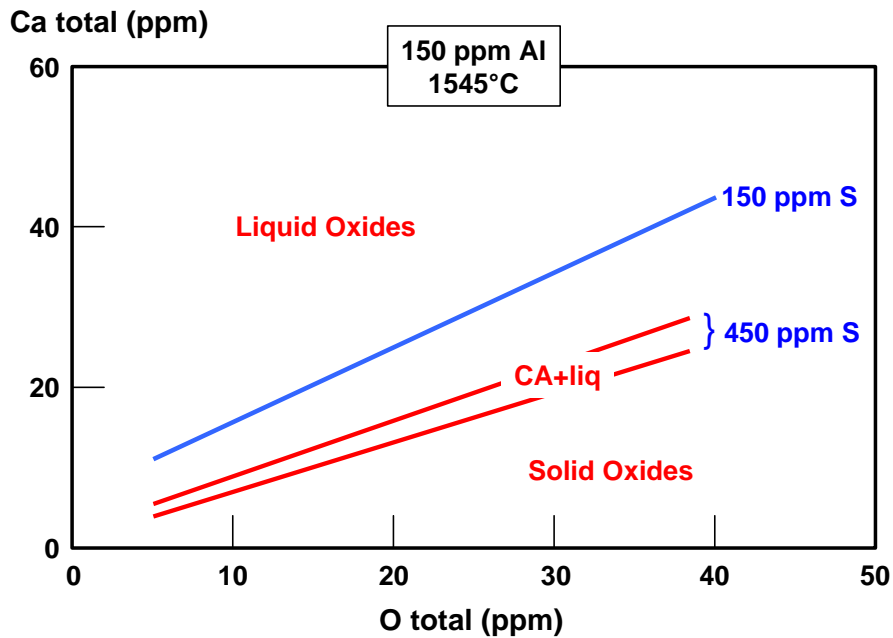


Figure 8 : Nature of oxide phases formed as a result of Ca treatment of a steel grade containing 150 ppm Al, as a function of Ca and O contents. The lines indexed with S content indicate the minimal value of Ca content leading to CaS precipitation in liquid steels, for the given S content.

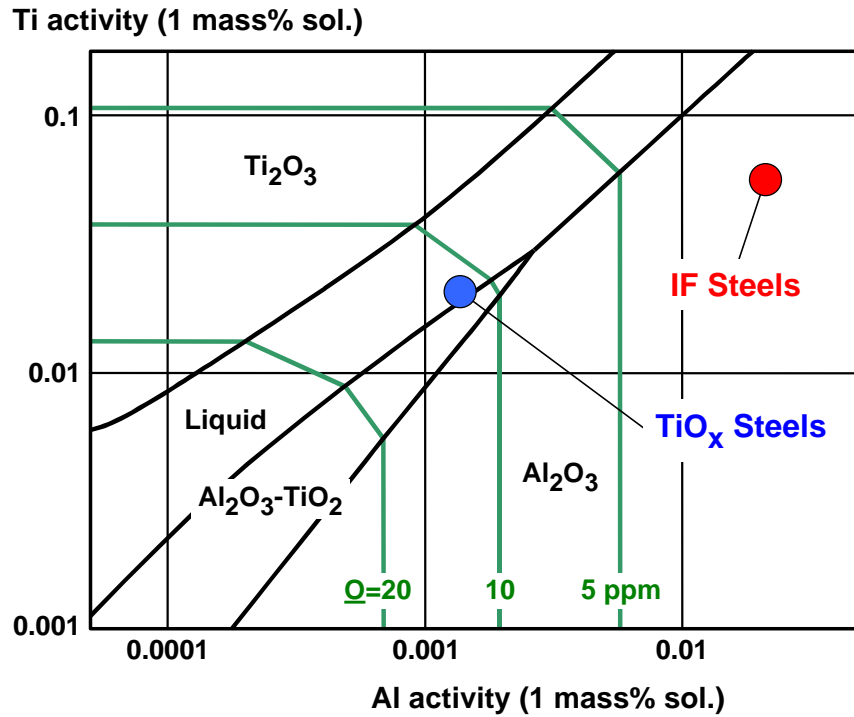


Figure 9 : Computed equilibrium diagram for the system Fe-Ti-Al-O at 1520°C.

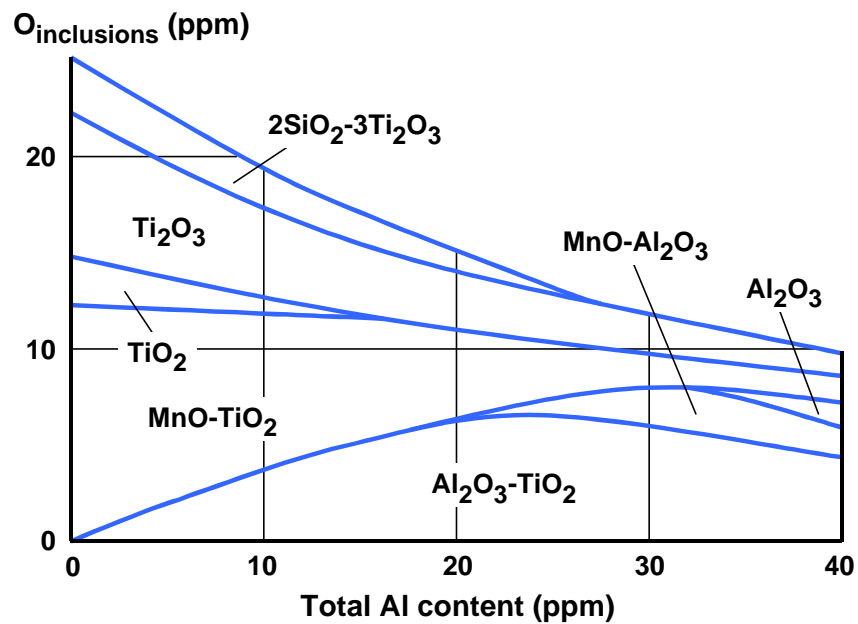


Figure 10 : Phases formed after complete crystallisation of inclusions formed at equilibrium during steel solidification.

Steel composition : 0,7%C-1,5%Mn-0.08%Si-150 ppm Ti- 0 to 40 ppm Al.

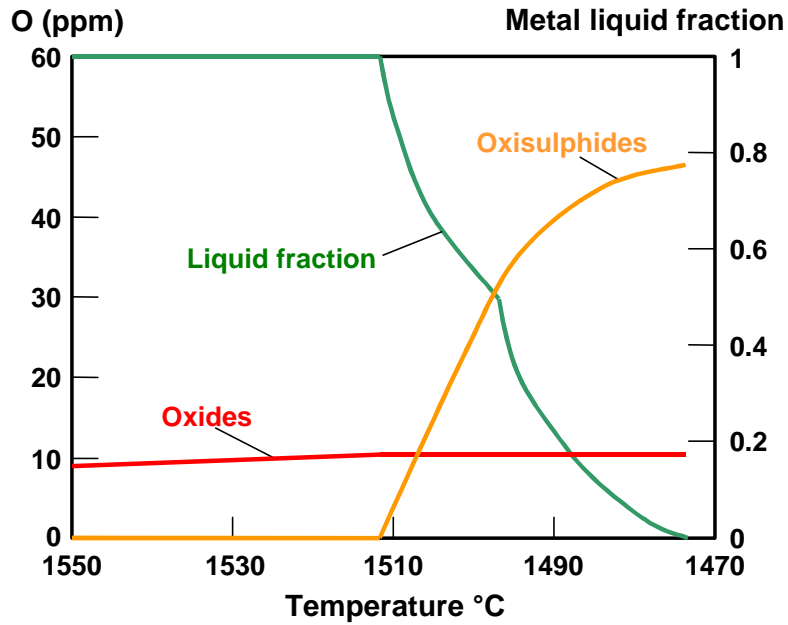


Figure 11 : Computed equilibrium sequence of precipitation of oxide and oxisulphide inclusions during steel solidification (amount of oxygen fixed in these inclusions) in a free cutting steel grade containing 60 ppm O.

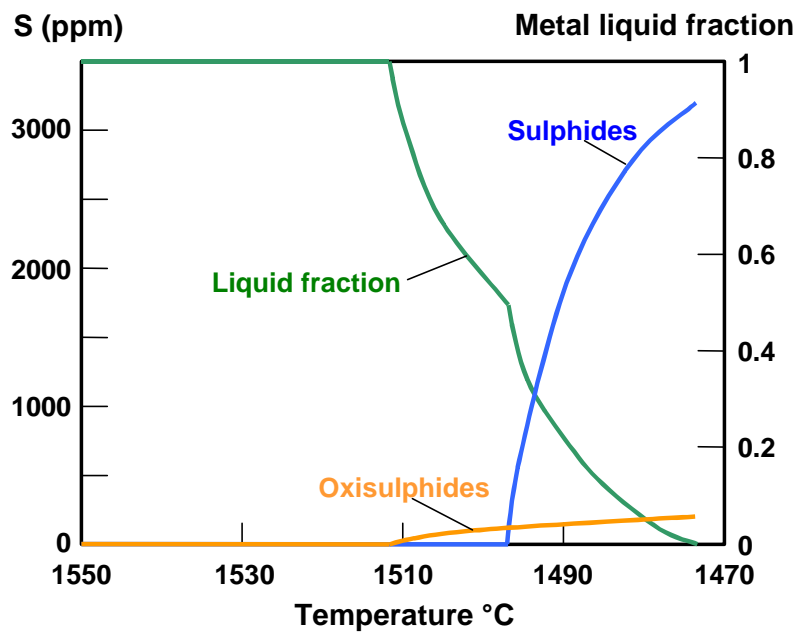


Figure 12 : Computed equilibrium sequence of precipitation of oxisulphide and sulphide inclusions during steel solidification (amount of sulphur fixed in these inclusions) in a free cutting steel grade containing 60 ppm O.

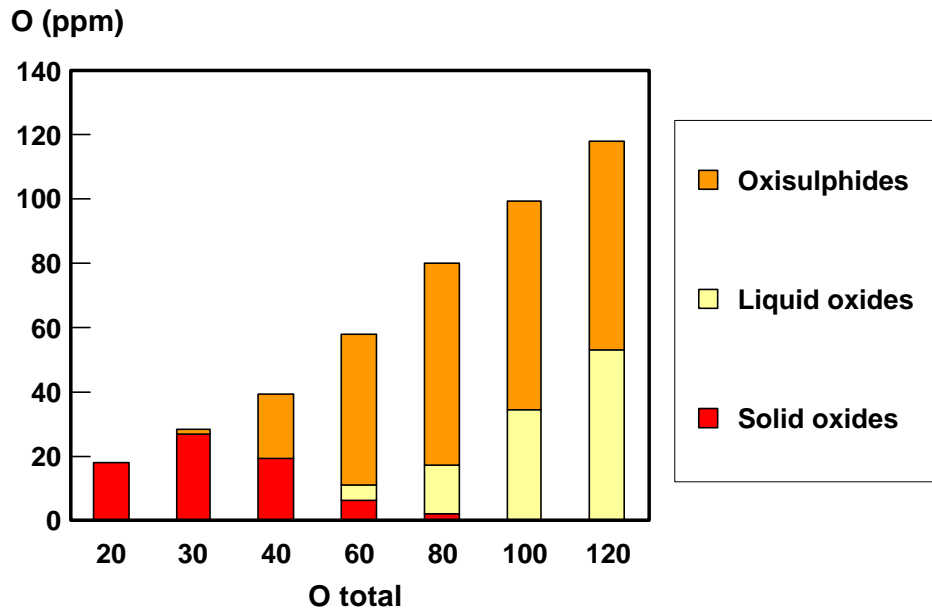


Figure 13 : Computed distribution of oxygen among oxide and oxisulphide inclusions, as a function of total oxygen content, in a free cutting steel.

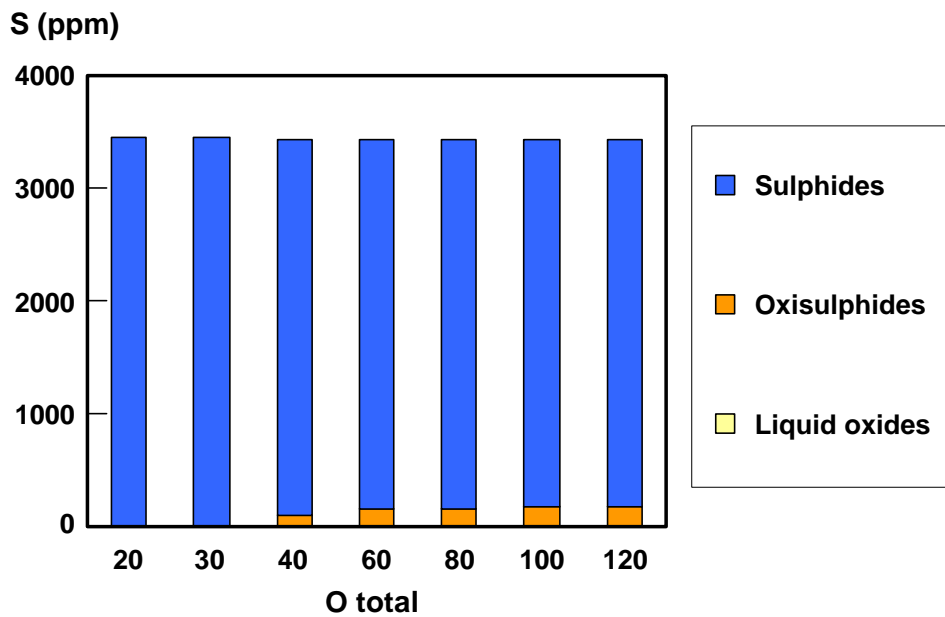


Figure 14 : Computed distribution of sulphur among oxisulphide and sulphide inclusions, as a function of total oxygen content, in a free cutting steel.