Fundamentals of High Temperature Processes

Reduction of manganese ores by methane-containing gas

N.ANACLETO et al.

Reduction of Groote Eylandt (Australia) and Wessels (South Africa) manganese ores using CH_4–H_2–Ar gas mixture was investigated in a fixed bed laboratory reactor in the temperature range 1 000–1 200°C. The extent and kinetics of manganese ore reduction as a function of gas composition and temperature were determined by on-line off-gas analysis using mass-spectrometer and dew point sensor. Morphology of ores and its change in the course of reduction was examined by optical and scanning electron microscopy. Phases of raw materials and reduced samples were analysed by XRD and EPMA.

Manganese and iron oxides were reduced to carbide $(Mn, Fe)_7C_3$. High extent and rate of reduction by methane-containing gas in comparison with carbothermal reduction were attributed to high carbon activity in the reducing gas, which was in the range 15–50 (relative to graphite). The reduction rate of Wessels manganese ore increased with increasing temperature. Reduction rate and extent of Groote Eylandt manganese ore achieved maximum at 1 050°C. The decrease in rate and extent of reduction of Groote Eylandt ore at higher temperatures, particularly at 1 150–1 200°C, was due to sintering and formation of semi-liquid silicate slag. An addition of lime (10–15 mass% CaO) to the Groote Eylandt manganese ore increased melting temperature of slag and significantly increased the rate and extent of reduction at elevated temperatures.

(cf. *ISIJ Int.*, **44** (2004), 1615)

Occurrence condition for a swirl motion of a bath agitated by bottom gas injection

M.IGUCHI et al.

A swirl motion of a cylindrical bath appears under a certain condition when the bath is agitated by bottom gas injection. The swirl motion can be classified into two types. One is called the shallow-water wave type, and the other is called the deep-water wave type. The condition for the occurrence of a swirl motion of the deep-water wave type was experimentally investigated based on water model experiments. Empirical equations were proposed for predicting the condition as functions of the gas flow rate, vessel diameter, inner diameter of the nozzle, and the physical properties of fluids.

(cf. *ISIJ Int.*, **44** (2004), 1623)

Numerical modeling of nucleation and growth of inclusions in molten steel based on mean processing parameters

J.ZHANG et al.

As an important aspect of inclusion engineering, numerical prediction of inclusion behavior in molten steel has attracted much attention in order to control inclusions in steel. Although considerable efforts have been made in the modeling of inclusion growth, it is still necessary to employ an initial particle size distribution (PSD) gained from experiments or assumptions as an input for numerical models. The present work focuses on the construction of a general nucleation-growth model, which combines thermodynamics, classical homogeneous nucleation theories and dynamics of particle collision and coagulation on the basis of mean processing parameters. This can be employed, without any initial PSD of inclusions in advance, to describe the time evolution of PSD in molten steel during inclusion nucleation, Ostwald ripening, and collision growth processes. With regard to collision-coagulation growth mechanisms of inclusions, four approaches, namely Brownian collision, turbulent collision, Stokes collision and gradient collision in laminar shear layers, have been investigated to estimate their role in the evolution of PSD during steel melt deoxidation process. In addition, an approximate numerical technique, termed the 'DS method', has been developed as a modification of the so-called (1) discrete-sectional representation and (2) Particle-Size-Grouping method in order for an efficient solution for population balance equations (PBE) at lower cost in CPU time. Finally, as an application of this general model, the evolution of nucleation and growth of alumina inclusions is demonstrated in the Fe–Al–O melt system. The predicted molten steel total oxygen and particle size distribution of alumina inclusions are compared with the experiment data cited from references.

(cf. *ISIJ Int.*, **44** (2004), 1629)

Modelling shrouded supersonic jets in metallurgical reactor vessels

A.R.N.MEIDANI et al.

The use of shrouded supersonic jets for enhancing the performance of top blown metallurgical reactors has been studied using BOF pilot scale facilities set up in the MMPC's water modelling laboratory. The experimental results for three different designs of shrouded supersonic jet nozzles have demonstrated that greater depths of penetration and reduced mixing times can be achieved with co-axial sub and supersonic jets flow. Dimensional analysis indicates that the depth of penetration of a gas jet into a liquid bath depends on the height, H, of the lance tip from the quiescent bath, the liquid's Froude, Reynolds and Weber numbers, reflecting the ratios of gravity, viscous and surface tension forces to the jet's inertial, or momentum, forces. Good agreement between the mathematical model and experiments were obtained in terms of predicted and observed depths of penetration. Further efforts have been made to study jet penetration into liquid metals. The effects of density of liquid metal and a wide range of gas flow rates on the penetration depth were investigated theoretically. The results confirm that jet penetration depth can be increased with increasing shroud gas flow rate and decreased bath density.

(cf. *ISIJ Int.*, **44** (2004), 1639)

Ironmaking

Exergy analysis of charcoal charging operation of blast furnace

H.NOGAMI et al.

Effective use of biomass resource is expected to be one of the solutions to the environmental problems, since a sort of biomass absorbs carbon dioxide through photosynthesis reaction. One of the possibilities to utilize such biomass resources is the replacement of coal and/or coke with charcoal. With nature of charcoal it is known that the hot metal quality can be improved as well as abatement of environmental impact through less slag generation and virtually no CO_2 and SO_2 emissions. This paper performed an exergy analysis on charcoal charged blast furnace. As a result, it is revealed that the charcoal system needs more enthalpy and exergy inputs than conventional ironmaking system while it produces more energy available in the other processes. This keeps exergy loss in charcoal system in the comparable level with the conventional system. The analysis shows that each process included in the system still has a possibility to be improved. Thus the performance of the charcoal system is expected to be equivalent to or even better than the conventional system. Therefore ironmaking system with charcoal charged blast furnace is expected to be a key technology to contribute environmental issues.

(cf. *ISIJ Int.*, **44** (2004), 1646)

Steelmaking

Nozzle clogging behaviour of Ti-bearing Al-killed ultra low carbon steel

S.BASU et al.

In the present work, attempt has been made to investigate the influence of Ti on the castability of Al-killed ultra low carbon (ULC) steel, and to establish the possible reasons for the inferior castability of the Ti-bearing ULC steel *vis-à-vis* Ti-free grades. The work also attempted to identify suitable countermeasures for prevention of inclusion deposition in the submerged entry nozzles (SEN) during continuous casting of Ti-bearing Al-killed ULC steels. Characteristics of inclusions in the submerged entry nozzle deposit and corresponding liquid steel and slag samples from RH degasser and tundish were investigated. The presence of small quantity of Ti-bearing alumina inclusion was identified to be responsible for the extensive melt freezing inside the SEN deposit and poor castability of Ti-bearing Al-killed ULC steels. The influence of all materials contacting liquid steel subsequent to the RH degassing, on the reoxidation behaviour and castability of liquid steel, was assessed from their chemical composition. The present investigation indicated that while reoxidation is bad for the castability of all Al-killed steels, it becomes worse in the case of Ti-bearing Al-killed steels, primarily due to the formation of Ti-bearing inclusions that promote large-scale melt freezing inside the nozzle deposits.

(cf. *ISIJ Int.*, **44** (2004), 1653)

Equations for the calculation of the thermo-physical properties of stainless steel

K.C.MILLS et al.

Equations have been derived to calculate values of the thermophysical properties of all stainless steels for temperatures between 300 and 1 800 K (austenitic 3 series, ferritic-4 series and precipita-

tion-hardened 6-series alloys). Values of the following properties are given in both figures and tables: density (ρ), thermal expansion coefficient (α), heat capacity (C_p), enthalpy (H_T-H_{298}), thermal conductivity (λ) and thermal diffusivity (a), electrical resistivity (R), viscosity (η) and surface tension (γ).

(cf. *ISIJ Int.*, **44** (2004), 1661)

Reoxidation of Al–Ti containing steels by CaO–Al_2O_3–MgO–SiO_2 slag

D.-C.PARK et al.

Reoxidation of liquid steel containing Al and Ti by 14%CaO–35%Al_2O_3–10%MgO–41%SiO_2 (in mass%) slag was investigated at 1 823 K with initial Al content of 820 mass ppm and Ti content varied from 100 to 500 mass ppm. It was observed that Al and Ti in the steel were simultaneously oxidized by SiO_2 in the slag, and the soluble oxygen was supersaturated during the course, particularly with respect to Al. Based on the experimental results, a new mechanism of the reoxidation reaction was proposed, which involves chemical reactions both at the metal/slag interface and in the bulk metal. Self-dissociation of SiO_2 into Si and O at the slag/metal interface was found to play an important role in both supersaturation of oxygen, and subsequent formation of complex oxide inclusions. Formation of inclusions having a two-layer structure where an Al_2O_3 core was enclosed by complex Al–Ti–O oxide was explained in relation with supersaturation of oxygen in the steel.

(cf. *ISIJ Int.*, **44** (2004), 1669)

Casting and Solidification

Cold isostatic pressing of alumina–graphite castables, a new technique to manufacture special refractories

R.EMADI et al.

The refractory materials of the special refractories like ladle shroud (LS) and submerged entry nozzle (SEN) should have adequate chemical and mechanical properties such as high temperature mechanical strength and thermal shock resistance. Currently, alumina, graphite and additives are mixed with a phenolic resin or coal tar pitch, packed into a molding frame by a jig, formed by cold isostatic pressing (CIP), dried and finally fired in a reducing atmosphere, usually under coke, at more than 1 000°C. The purpose of this research is to introduce a novel technique to provide LS and SEN from alumina-graphite castable refractories by using CIP without a need to firing under reducing atmosphere. Compositions in relation to physical-mechanical properties are investigated and mixtures like 55% alumina, 20% refractory cement, 15% graphite, 5% micro silica and 6–8% water have shown to be promising and giving suitable results.

(cf. *ISIJ Int.*, **44** (2004), 1679)

A two-dimensional finite element thermomechanical approach to a global stress–strain analysis of steel continuous casting

M.BELLET et al.

This paper addresses the two-dimensional finite element simulation of steel continuous casting using a global non steady-state approach. The method aims at the calculation of the thermomechanical state (temperature, deformation, stresses) of steel all along the continuous casting machine. Both plane deformation and axisymmetric versions have been developed. The first one addresses the simulation of continuous casting of slabs, taking into account the possible curvature of the machine, whereas the second one applies to cylindrical billets. The implementation of the method is validated by comparison with results from the literature. It is applied to the study of a slab continuous caster for which successive depressive and compressive stress states are revealed in the secondary cooling region.

(cf. *ISIJ Int.*, **44** (2004), 1686)

Real-time analysis on non-uniform heat transfer and solidification in mould of continuous casting round billets

Y.MAN et al.

It is very important to obtain the temperature and heat flux distribution in the mould which can reflect the nonuniformity along circumferential direction and the changes of practical operation parameters for visualization of continuous casting process, on-line monitoring of strand quality and precise prediction of abnormality. In this paper, based on the data of continuous monitoring temperature in round billet casting machine, an inverse problem algorithm is applied to study the 3D heat flux field and the real 3D shell thickness profile in the mould which can reflect the nonuniformity of heat transfer along circumferential direction in normal production. The results indicate that under the course of normal production, the mould heat flux and shell thickness are various along the circumferential direction, and are influenced by the installation conditions of mould in caster. A "high heat flow region" occurs in the area 80–130 mm below meniscus, where the heat flux is obviously higher and more nonuniform than that in the area in middle and lower part of the mould. The heat flux profile along circumferential direction in the "high heat flow region" determines the profiles of shell thickness at different heights below meniscus to some extent, both of them have similar profiles, this provides theoretical basis for improving the billet surface quality and getting uniform shell thickness by analyzing and monitoring heat flux distribution in the mould especially in the "high heat flow region".

(cf. *ISIJ Int.*, **44** (2004), 1696)

Mechanism for loss of hot ductility due to deformation during solidification in continuous casting of steel

F.ZARANDI et al.

Strand surface cracking is a problem that can lead to scrap the product of the continuous casting process. Stress and strain developed during continuous casting have been found to be effective in this respect. The crack susceptibility is usually evaluated by assessing the steel hot ductility at the straightening stage of the process. The hot ductility of two Nb-microalloyed steels was evaluated in *in situ* melted specimens. The billet surface thermal history was simulated in order to generate the billet surface microstructure. The effect of deformation incorporated with steel solidification was studied and it was found that any kind of deformation during solidification results in loss of hot ductility. Metallography of specimens revealed that deformation caused grain boundary cracking and changed the segregation pattern, leading to loss of hot ductility. Based on this, a mechanism for hot ductility loss was proposed.

(cf. *ISIJ Int.*, **44** (2004), 1705)

Generation of hydrogen gas from solidified shell surface at initial stage of solidification of carbon steel

H.MIZUKAMI et al.

The generation of hydrogen gas from the surface of solidified shell of carbon steel was confirmed by the experiments of both collecting gas from shell surface using the sintered chill plate made of stainless steel and measuring temperature in the copper chill plate at initial stage of solidification. The hydrogen gas existed in collected gas and the amount of hydrogen gas increased with increasing hydrogen content in molten steel. The temperature in chill plate became high because the ratio of hydrogen gas of which thermal conductivity was large existed in the gap between shell and chill plate and the heat transfer from shell to chill plate became large when the hydrogen content in molten steel was high. When the hydrogen gas generated from shell surface blocks flow of mold flux into the gap, the possibility of sticker breakout in continuous casting would increase.

(cf. *ISIJ Int.*, **44** (2004), 1714)

Welding and Joining

Laser beam welding of 2205 duplex stainless steel with metal powder additions

H.C.WU et al.

Laser beam welding with the aid of metal powder additions to the weld pool was carried out to modify the ferrite/austenite (α/γ) ratio of the weld metal of 2205 duplex stainless steel (DSS). The α content in the weld metal of DSS welds could be controlled by the proper flow rate of nickel powder through a coaxial nozzle. This process had the advantage of using only a small amount of filler metal, *i.e.* a few grams per minute of nickel powder, in the welding process. Imapct and notched tensile tests were utilized to evaluate mechanical properties of laser welds. The notched tensile test was also carried out in hydrogen under a slow displacement rate. The susceptibility to hydrogen embrittlement (HE) was estimated from the loss in notched tensile strength and correlated with the microstructure of a given laser weld. On the whole, the susceptibility to HE decreased with increasing the γ content of DSS welds. Autogeneous laser welds containing the highest α content of all welds tested were most susceptible to HE. The base material with banded $\alpha+\gamma$ structures was susceptible to HE and exhibited severe secondary cracks mainly along α/γ phase boundaries. Although laser welds produced at a flow rate of 3 g/min nickel powder had similar α content to the base material, they were more resistant to HE owing to randomly distributed α

and γ phases in the weld metal. The impact energy of laser welds at low temperatures (−75 to −100°C) along with the hardness test could also be used to check if the proper amount of nickel powder was added in laser welding of DSSs.

(cf. *ISIJ Int.*, **44** (2004), 1720)

Surface Treatment and Corrosion

Corrosion behavior of 55mass%Al–1.6mass%Si–Zn alloy in wet–dry cyclic environment

A.P.YADAV et al.

The corrosion of 55mass%Al–1.6mass%Si–Zn (GL) alloy has been tested under a wet–dry cyclic condition using an AC impedance technique to clarify its corrosion behavior. The results have been compared with that of a zinc sample exposed under identical condition. The sample was exposed to alternate conditions of immersion for 1 h in a 0.05 kmol/m^3 NaCl solution and drying for 7 h at 298 K and 60% RH, and the corrosion rate was monitored for 10 d (30 cycles) using a two-electrode type probe. Simultaneously, the corrosion potential was continuously monitored using a special arrangement in combination with a Luggin probe tip. From the monitoring results of the corrosion rate and corrosion potential and the polarization curve, it was found that the corrosion rate of GL was decreased by inhibition of the cathodic reaction.

The impedance response was evaluated by using an equivalent circuit considering the charge and mass transfer consequences of the coupled corrosion processes. It was found from the time constant of the diffusion impedance that the corrosion product layer formed on GL alloy acted more effectively as a diffusion barrier against oxygen transport compared to zinc.

(cf. *ISIJ Int.*, **44** (2004), 1727)

Transformations and Microstructures

Texture evolution during the processing of electrical steels with 0.5% Si and 1.25% Si

M.F.CAMPOS et al.

The development of the crystallographic texture in the processing of a 0.5% Si semi-processed steel sheet has been investigated. The results were also compared with those of a steel with 1.25% Si and 0.22% Al, to verify the effect of the chemical composition. The texture was examined after the following steps: i) hot band ii) 80–90% cold reduction iii) annealed iv) after skin pass v) after final annealing. The texture is very similar for both chemical compositions. The hot band presents an almost random texture. After 80–90% cold reduction, a typical rolling texture of steels is observed, containing the fibers ⟨110⟩//RD and ⟨111⟩//ND. After annealing, the fiber ⟨111⟩//ND is the most important component, but now with maximum at {111}⟨112⟩. After skin pass and final annealing, the main components are the fiber {111}⟨*uvw*⟩ and Goss (110)[001]. The results indicate that the Goss intensity tends to increase for smaller values of skin pass (where final grain size also increases). The change of Si content (from 0.5% up to 1.25% Si) and of Al (from ~0 upto 0.22%) did not produce significant variation about the texture components.

(cf. *ISIJ Int.*, **44** (2004), 1733)

Thermodynamic analysis of the Fe–Al–C ternary system by incorporating *ab initio* energetic calculations into the CALPHAD approach

H.OHTANI et al.

A thermodynamic analysis of the Fe–C–Al ternary system has been carried out covering a wide range of temperatures and composition. Special care was taken to the expression of the free energy for the ternary Perovskite carbide phase, Fe_3AlC (κ), by considering the crystallographic similarity between the κ phase and the $L1_2$ structure. The free energy was calculated using the $(Fe,Al)_3(Fe,Al)_1(C,Va)_1$ sublattice model, and the κ and $L1_2$ structures were treated as a continuous solution. Because of the lack of experimental information available, the thermodynamic properties of the $E2_1$ structure were evaluated using the Full Potential Linearized Augmented Plane Wave (FLAPW) method.

The *ab initio* energetic calculations show that the stable $E2_1$ structure of the κ phase is highly preferred compared with the metastable Fe_3Al–$L1_2$ structure. Contour plots of the charge density for the κ phase indicate that the bonding between the Fe and C atoms forms in the Fe_3AlC–$E2_1$ structure, and that this interaction between the atoms enhances the energetic stability of the κ phase.

According to our phase diagram calculations, the κ phase is in equilibrium with the fcc Fe, B2-type intermetallic compound, as well as the graphite phase. This finding is in good agreement with previous experimental results.

(cf. *ISIJ Int.*, **44** (2004), 1738)

Microstructure evolution of iron carbide during reaction with steam at elevated temperatures

M.HISA et al.

Cross-sectional microscopy and X-ray diffractometry in combination with thermogravimetry were conducted to investigate the microstructure evolution of iron-ore derived iron carbide caused by the reaction with steam at elevated temperatures. During continuous heating from 393 to 1373 K at 10 K min^{-1}, the microstructure of the iron carbide changed in the following sequence: (1) densification due to oxidation of Fe_3C, (2) coarsening by decomposition of Fe_3C and by reduction of iron oxides, and then (3) re-densification associated with oxidation of Fe. The microstructure evolution was found to correspond well to the volume change due to the phase transformations of the iron carbide. Graphite formed in the iron carbide as a result of decomposition of Fe_3C seems to have a highly crystallized lattice that contracts in its *c*-axis direction.

(cf. *ISIJ Int.*, **44** (2004), 1748)

Mechanical Properties

Cross-weld creep behavior and life prediction of low alloy ferritic steels

S.FUJIBAYASHI et al.

The reliability of elevated temperature components depends upon understanding the creep behavior of welds, which often determine the components' lives. The most likely manner of failures at high temperatures for the serviced welds fabricated from low alloy ferritic steels should be Type IV cracking. In the present work using 1.25Cr–0.5Mo and 2.25Cr–1Mo steel welds, however, the location and the morphology of the ultimate failures were influenced by a couple of factors, namely, the magnitude of stress, temperature, time to rupture, specimen geometry and inherent creep properties owned by each alloy. Thus, the consistent relationship between the feature of creep damage and the life consumption to be utilized for the remnant life assessment of welds has not been derived.

As the alternative, the authors have examined the cross-weld creep behavior at the tertiary creep stage. Despite the variation of failure types, which were Type I, Type III, Type IV and ductile rupture at the parent material, the omega method predicted the rupture life with the accuracy of a factor of 2. Furthermore, it was found that the linear relationship between ε and $\dot{\varepsilon}$ appearing at the tertiary creep stage was also available in the life prediction. The slope of strain rate *versus* strain derived from the above relationship was correlated with the rupture life independently of failure types, specimen geometry and materials and the same level of accuracy as that of the omega method was obtained. From the usefulness of this technique and observation of grain boundary damage at the Intercritical HAZ (ICZ), the authors has interpreted that grains around creep cavities are still subjected to a significant level of stress, suggesting that apparent feature of grain boundary damage dose not necessarily exhibit the remaining creep strength of welds.

(cf. *ISIJ Int.*, **44** (2004), 1753)

Effect of Y–Ce complex modification on thermal fatigue behavior of high Cr cast hot working die steels

Q.C.JIANG et al.

The effect of Y–Ce complex modification on the thermal fatigue (TF) behavior of cast hot working die steels was investigated and the mechanism of Y–Ce action was discussed. The experimental result showed that TF behavior of the steel modified by Y–Ce complex modification under thermal cycling temperatures of 650–25°C was over 1.5 times than that of the unmodified, which is likely due to the enhancing of the resistance to oxidation. At the same time, after the Y–Ce complex modification, impact toughness was also increased by nearly 200%, which is mainly attributed to the great improvement of the morphology and distribution of inclusions and the reduction of their amount.

(cf. *ISIJ Int.*, **44** (2004), 1762)

Physical Properties

Adhesion of enamel layer at repeated firings in Ti-stabilized IF steel sheet for porcelain enamel and its mechanism

Y.ISHIGURO et al.

Adhesion of enamel layer in Ti-stabilized Intersti-

tial-Free steel (Ti-IF) for porcelain enamel was studied through pickling loss weight, smuts on a pretreated Ti-IF steel, chemical compositions of steel and the repeated number of firing to form enamel, comparing with high oxygen steel for porcelain enamel.

When pickling loss weight in Ti-IF steel is below 30 g/m^2, the adhesion of enamel layer can be over 80% even after firing is repeated four times. High oxygen steel, in contrast, has over 80% adhesion of enamel layer, regardless of the repetition of firing, and its adhesion is not related to pickling loss weight.

TEM observation reveals that the smut on pretreated Ti-IF steel is mainly round-shaped TiS (100–300 nm) and the one on pretreated high oxygen steel is mainly Cr_2MnO_4 (100–300 nm). During the reaction between enamel and pretreated steel for firing process, TiS is presumed to worsen adhesion, while Cr_2MnO_4 is not related to adhesion. Therefore, reducing TiS (lowering pickling loss weight) is an effective measure to keep satisfactory adhesion in Ti-IF steel at repeated firings.

Under conventional pretreatment conditions (ex. pickling for about 5 min with 12–15% H_2SO_4 at 70–80°C and Ni-deposition for about 5 min with 13–18 g/L $NiSO_4 \cdot 7H_2O$ at 70–80°C), Cu should be higher than about 0.04% and P should be lower than about 0.013% to be below 30 g/m^2 as pickling loss weight in order to keep over 80% adhesion in Ti-IF steel.

(cf. *ISIJ Int.*, **44** (2004), 1767)

Social and Environmental Engineering

Thermodynamic analysis on the dust generation from EAF for the recycling of dust

Y.KASHIWAYA et al.

Recently, in addition to the large interest on the CO_2 emission problem, the energy saving and the environmental conservation become more and more important issue. Zero emission campaign is adopted by many companies. In such circumstances, most of steel companies were carrying out the recycling of dust by many ways. There are many aspects on the dust recycling. One of important purpose is the zinc recovery, and other is the utilization as a slag (*e.g.* roadbed material) by injection. Especially for the dust injection, many troubles such as an accumulation in the filtering system and an increase of the content of harmful elements in the dust will occur. Then, it become very important to understand the mechanism and the thermodynamics of the dust generation or/and precipitation form EAF to prevent those troubles.

In this study, the dust sampled from the impeller of blower in the dust filtering system of EAF was examined by XRD and XRF. Quite complicated compounds formed in Zn–Fe–Pb–Cr–Mn–O–Cl–F system were found in the dust according to the dust injection. Thermodynamic analysis was performed and the equilibrium composition obtained from the calculation was in excellent agreement with the actual composition in the dust. Main constituents in the dust are $ZnFe_2O_4$ and Fe_2O_3. Relatively dominant ones are as follows: Fluorides are FeF_3, ZnF_2 and PbF_2, chlorides are $ZnCl_2$ and $PbCl_2$, and oxides are ZnO and MnO_2. The fluorides deposit around 1 000°C from gas phase. And the chlorides ZCl_2, $PbCl_2$ and oxides MnO_2 form less than 500°C. The partial pressure of chloride gas will become a maximum around 400°C, when there is no moisture.

(cf. *ISIJ Int.*, **44** (2004), 1774)