

Fundamentals of High Temperature Processes

Equilibrium between dissolved chromium and oxygen in liquid high chromium alloyed steel saturated with pure Cr₂O₃T.ITOH *et al.*

Equilibrium between Cr and O in the high Cr steel melt is one of the most important information to control Cr content in the stainless steel. In spite of such importance, there are some uncertainties in the literature values including the recommended values of the Japan Society for the Promotion of Science (JSPS) on deoxidation equilibrium constant and interaction parameters. The main reason of such uncertainties of the previous works is referred to the insufficient consideration on the thermodynamic properties of oxide phase in equilibrium with liquid Fe-Cr alloy. The present work deals with the equilibrium relation between dissolved Cr and O in liquid high Cr steel saturated with pure solid Cr₂O₃.

The equilibrium constant of reaction and the interaction parameter between Cr and O in liquid iron saturated with pure solid Cr₂O₃ is given by the following equations in the present work.

$$\begin{aligned} \text{Cr}_2\text{O}_3(\text{s}) &= 2\text{Cr} + 3\text{O} \\ \log K &= -36200/T + 16.1 \quad (1823\text{ K} < T < 1923\text{ K}) \\ e_{\text{O}}^{\text{Cr}} &= -123/T + 0.034 \\ &(\text{mass}\% \text{Cr} < 46, 1823\text{ K} < T < 1923\text{ K}) \end{aligned}$$

The activity of O can be expressed by above thermodynamic function without the second order interaction parameter up to 46 mass%Cr.

(cf. *ISIJ Int.*, **40** (2000), 1051)Activities of the constituents in spinel solid solution and free energies of formation of MgO, MgO·Al₂O₃K.FUJII *et al.*

Spinel (MgO·Al₂O₃) is known as one of the most harmful non-metallic inclusions in steel. However, the technology to avoid spinel formation has not yet been established due to lack of thermodynamic information on the spinel itself. In the present work, the free energies of formation of MgO and MgO·Al₂O₃, and the activities of the constituents in spinel solid solution have been directly measured by the chemical equilibrium technique. The free energies of formation of MgO and MgO·Al₂O₃ determined in the present work are expressed by the following equation:

$$\begin{aligned} \text{Mg}(\text{l}) + 1/2 \text{O}_2(\text{g}) &= \text{MgO}(\text{s}) \\ \Delta G_{\text{f,MgO}}^\circ &= -669350 + 135.07T \quad (\text{J/mol}) \\ \text{Al}_2\text{O}_3(\text{s}) + \text{MgO}(\text{s}) &= \text{MgO} \cdot \text{Al}_2\text{O}_3(\text{s}) \\ \Delta G_{\text{f,MgO} \cdot \text{Al}_2\text{O}_3}^\circ &= -20790 - 15.77T \quad (\text{J/mol}) \end{aligned}$$

The activity of stoichiometric MgO·Al₂O₃ exhibits negative deviation from ideality in the spinel solid solution. Phase stability diagram of spinel formation in liquid steel was assessed as a function of aluminum, magnesium and oxygen contents in iron at 1873 K. The predicted phase boundaries of MgO·Al₂O₃, MgO and Al₂O₃ agreed well with previous observations by one of the present authors.

(cf. *ISIJ Int.*, **40** (2000), 1059)

Ironmaking

Significance of pressure, temperature and reaction rate events in a blast furnace simulation test

P.C.PISTORIUS *et al.*

The condition of iron ore samples in blast furnace simulation tests according to the REAS procedure was determined by interrupting the test at different stages close to the maximum in the pressure drop across the sample bed. While the onset of the pressure increase does agree with liquid formation (melting of fayalite), the increase in the pressure drop appears to be related to sample compaction (softening). Elimination of pores formed by reduction (rather than lubrication by liquid) appears to be the main factor affecting compaction. The first strong temperature arrest is not associated with melting of the slag phase, but rather with the onset of (endothermic) direct reduction.

(cf. *ISIJ Int.*, **40** (2000), 1067)

The effects of operational parameters on the transport phenomena in COREX melter-gasifier

S.-C.LEE *et al.*

Using a computational code developed for simulating the COREX melter-gasifier, the effects of operational parameters on the transport phenomena in the melter-gasifier were studied. The parameters studied were the bed height, C/O ratio, operating pressure and steam injection ratio. When the bed height was increased, the temperature near the combustion zone also increased due to there being sufficient heat exchange between the gas and solid phase. However, the freeboard zone temperature remained constant due to the increased residence time for heat exchange. Operational pressures affect the rate of tar in the coal. However, the extent of the change in the evolved tar as a function of pressure did not vary severely. The variation in the C/O ratio affected the heating rate of coal followed by a drastic change in the heat and mass transfer of solid and gas phases. The combustion zone and the freeboard zone temperature were changed largely by variations in the C/O ratio. The C/O ratio also changed the evolution rate of the coal by the changes in heating rate. From these considerations, the C/O ratio should be carefully controlled for the stable operation. The effects of steam injection into the melter-gasifier were also studied. Up to a steam injection rate of 30%, the temperature of the combustion zone increased. Steam injection also affected the effluent composition of the gas phase. When the steam injection ratio was increased, the CO/CO₂ ratio was decreased while H₂/H₂O ratio was remained unchanged.

(cf. *ISIJ Int.*, **40** (2000), 1073)

Steelmaking

A thermodynamic and kinetic model of reoxidation and desulphurisation in the ladle furnace

M.A.T.ANDERSSON *et al.*

A thermodynamic and kinetic model of reoxidation and desulphurisation in the ladle furnace has

been developed by using a two-dimensional fluid-flow model combined with equations expressing the thermodynamics of reoxidation and desulphurisation. More specifically, ladle vacuum treatment of a gas-stirred ladle has been simulated. In order to describe the activities of the oxide components of the slag, expressions by Ohta and Suito¹⁾ were adopted. The thermodynamic model describes the slag/metal equilibria between Al, Si, O, Mn and S in the molten steel and Al₂O₃, SiO₂, FeO, MnO and S in the slag. A fluid dynamic model that considers the slag, steel and argon phases derives the kinetics. Results from an isothermal calculation have been heuristically compared with industrial plant data and they show good agreement. The model results have also revealed that the reduction of silica plays a part in aluminium loss during ladle treatment.

(cf. *ISIJ Int.*, **40** (2000), 1080)

Modeling of a DC electric arc furnace—heat transfer from the arc

J.ALEXIS *et al.*

A mathematical model describing heat and fluid flow in an electric arc has been developed and used to predict heat transfer from the arc to the steel bath in a DC Electric Arc Furnace. The arc model takes the separate contributions to the heat transfer from each involved mechanism into account, *i.e.* radiation, convection, condensation and energy transported by electrons. The model predicts heat transfer for different currents and arc lengths. Model predictions show that arc efficiency is higher for lower power input. The model also predicts shear stresses and current density distribution at the steel surface. This information can be used as boundary condition input to simulate the effect of heating with electrodes in a DC EAF on the heat and fluid flow in the steel bath.

(cf. *ISIJ Int.*, **40** (2000), 1089)

Heating and electromagnetic stirring in a ladle Furnace—A simulation model

J.ALEXIS *et al.*

A three-dimensional simulation model coupling heating and induction stirring in an ASEA-SKF ladle furnace was developed. Data of the heat transfer from the arcs to the steel bath were predicted in a separate model and included as boundary conditions in a ladle model. The arc model considers the contributions of heat transferred by of each of the following mechanisms: radiation, convection, condensation and energy transported by electrons. Predictions were made to simulate the change of temperature distribution in the ladle during simultaneous heating with electrodes and stirring by induction. A first attempt was made to compare the predictions with measured temperatures from a 100t ASEA-SKF ladle. The agreement was found to be fairly good when heat-flux data for a 25 cm arc length were used as input to the ladle model. This indicates that the model can be used for more in-depth studies of the effects of heating for ladles that are inductively stirred.

(cf. *ISIJ Int.*, **40** (2000), 1098)

Casting and Solidification

Mathematical modeling of fluid flow phenomena during tundish filling and subsequent initial casting operation in steel continuous casting process *C.-M.FAN et al.*

The purpose of this study is to develop a mathematical model to analyze the fluid flow phenomena of molten steel in the tundish during its filling stage and subsequent initial casting operation in the continuous casting process of steel. The ultimate goal is to assure smooth initial casting operation without nozzle clogging by avoiding high deposition rate of inclusion on any of the tundish outlets during tundish filling and subsequent initial casting operation.

The mathematical model is developed based on a computational fluid dynamics technique, named SOLA-MAC, and the $k-\epsilon$ two-equation turbulence model. SOLA-MAC technique has the ability to handle the flow problem encountered in tundish filling, which is a transient flow problem with highly distorted free surfaces and the locations of the free surfaces are to be determined by theory. A fluid particle method is also employed in this study to analyze the distribution of inclusions in the molten steel and the extent of inclusion contamination in various strands of the continuous casting tundish. A water model that is one-fourth the scale of an actual billet continuous caster is also constructed in this study. Water model experiments are conducted to verify the accuracy and reliability of the mathematical model.

The developed model is first tested on the water model to calculate the flow pattern of water in the tundish during the very early stage of filling operation. The simulated filling patterns are compared to the water model experiments. Good consistency is observed. The model is then tested on an actual billet continuous caster with four strands to simulate the fluid flow phenomena of molten steel in the tundish during the filling and subsequent initial casting operations. Inclusion distribution and the extents of inclusion contamination among the outlets of the various strands in the tundish are also analyzed. The simulated results show that for the left half of tundish, inclusion contamination in #2 strand is significantly more severe than that in #1 strand. This is confirmed by the actual experience on the shop floor of that particular billet caster that #2 strand experiences more difficulty in clogging problem during the initial casting operation than #1 strand does.

(cf. *ISIJ Int.*, **40** (2000), 1105)

Forming Processing and Thermomechanical Treatment

Prediction of transient slab temperature distribution in the re-heating furnace of a walking-beam type for rolling of steel slabs

J.G.KIM et al.

This article is on heat transfer analysis by the commercial code, FLUENT, for slabs heated in a walking-beam type of a re-heating furnace in POSCO (Pohang Iron & Steel Co., Ltd.). Steady

state, three-dimensional analysis is performed for turbulent reactive flow and radiative heat transfer in the furnace. Computation is based on the Favre-averaged conservation equations of mass, momentum, energy and species with the $k-\epsilon$ turbulence model. The predicted global energy flow is in good agreement with the measurement. Two-dimensional transient calculation is performed for conduction in a slab with the boundary condition given in terms of the calculated local heat flux in the furnace. Results show substantial variation of the temperature across the furnace as well as between skid and non-skid regions in the slab. Parametric study is performed to examine skid mark severity and energy loss to the skid system with respect to the height and shape of the skid button and the convective heat transfer coefficient to cooling water. It is shown that the radiative exposure, which depends on the height and shape of the skid button, reduces skid mark severity by decreasing heat loss from the slab. The convective heat transfer coefficient to the cooling water turns out not to be of as much significance to skid mark severity as the exposure area of the skid button.

(cf. *ISIJ Int.*, **40** (2000), 1115)

Shape memory effects in an Fe14Mn6Si9Cr5Ni Alloy for Joining Pipe

J.C.LI et al.

The shape memory effect (SME) of an Fe14Mn6Si9Cr5Ni alloy has been studied, and resulted to be the best for joining pipe. Training can improve the SME of the alloy. Fe14Mn6Si9Cr5Ni alloy shows good creep and stress relaxation resistance. Its corrosion resistance in alkaline solution is 4–5 times better than that of 304 and 316 stainless steels. The tensile force of 20 KN and sealing pressure of 6 MPa can satisfy usual requirements for joining pipe in general industrial applications.

(cf. *ISIJ Int.*, **40** (2000), 1124)

Surface Treatment and Corrosion

Mechanism and prevention of edge over coating in continuous hot-dip galvanizing

Y.TAKEISHI et al.

In order to clarify the mechanism of edge over coating (EOC) for continuous hot-dip galvanizing, a visualization test of the gas flow on strip and a cold model test to measure the profile of the coating thickness at the strip edge were carried out. Outward deflected gas flow was observed at the strip edge and EOC developed in the absence of gas wiping. With gas wiping, EOC developing below the wiping position is reduced by the impinging pressure of the gas wiping jet, and the film thickness becomes approximately uniform at the gas wiping position. However, upward of the gas wiping position, EOC increases again and the outward deflected gas flow on the strip edge sweeps the liquid film to the strip edge. EOC is considered to develop at the location where the dynamic pressure of the outward deflected gas flow balances with the surface tension.

For the prevention of EOC, edge masking was devised and the effects which reduce EOC were mea-

sured in the cold model test and on a commercial line test. The edge mask which can be kept farther away from the strip edge is more effective for preventing EOC than the edge plates. The optimum dimension of the edge mask is 30 mm in width and 75–100 mm in depth, and installing it at 4–10 mm away from the strip edge is most effective. It was confirmed by the commercial line test that the edge mask can reduce EOC from 45% to less than 10%.

(cf. *ISIJ Int.*, **40** (2000), 1127)

Effect of δ -ferrite on sulfide stress cracking in a low carbon 13 mass% chromium steel

T.HARA et al.

It is important for the 13 mass% chromium steels to keep the passivation in order to improve SSC (Sulfide Stress Cracking) resistance in sour environments. For example, the addition of molybdenum and chromium is effective to keep the passivation. However, when these elements are excessively added, δ -ferrite is formed. Therefore, the effect of δ -ferrite on SSC in the low carbon 13 mass% chromium steels was investigated. SSC occurred in the case that δ -ferrite is formed to some extent because the corrosion potential was lowered to that of the active state. The occurrence of SSC did not depend on the difference of shape of δ -ferrite. The reason for the difference in corrosion potential with and without δ -ferrite is attributed to the existence of a chromium depleted zone due to the precipitation of chromium carbides or nitrides near the δ -ferrite.

(cf. *ISIJ Int.*, **40** (2000), 1134)

Transformations and Microstructures

Estimation of number of precipitate particles per unit volume from measurements on polished specimen surfaces—computer simulation

A.UMEZAKI et al.

In studies of phase transformation kinetics a stereological analysis is often employed to determine the number of precipitate particles in the specimen volume from particle numbers measured on polished surfaces. Possible sources of error in applying Schwartz-Saltykov diameter analysis to measurements in actual microstructures were studied by computer simulation. Particles were generated in a fixed volume and their sizes were increased at prescribed nucleation and growth rates. The number and size distribution of sections were measured on random planes and the temporal variation of particle numbers per unit volume was calculated. It is demonstrated that the uncertainty of D_{max} , the maximum particle size to be determined from microstructure in each measurement, does not cause an appreciable amount of error if D_{max} is less than 3–5 times the actual maximum particle size. The increase in size and impingement of particles can produce a very different temporal variation of apparent particle numbers on the plane of polish from the variation of actual particle numbers in the specimen volume. The non-sphericity of particles, especially particles elongated in one direction (e.g. prolate ellipsoids), may cause a significant amount of error if they are treated as spherical particles.

(cf. *ISIJ Int.*, **40** (2000), 1142)

Deformation microstructure and tensile strength of cold rolled pearlitic steel sheets

S. TAGASHIRA et al.

The deformation microstructure produced by heavy cold rolling (from 70% to 95% reduction) of pearlitic structure with various amounts of rolling and the tensile strength of the cold rolled sheets were studied in the plain carbon steels with various carbon contents (0.6, 0.76, and 1.0 mass% C). The deformation microstructure was classified into the following three types; 1) Irregularly Bent Lamella (IBL): lamellae originally inclined with large angles to the rolling plane and irregularly bent after deformation, 2) Coarse Lamella with Shear band (CLS): the rhomboidal blocks of weakly deformed lamellae bounded by shear band, 3) Fine Lamella (FL): heavily deformed lamellae aligned parallel to the rolling direction with fine interlamellar spacings. As rolling reduction increases, the proportion of FL increases.

The tensile strength of cold rolled specimens increases with rolling reduction. Work hardening with respect to true strain by cold rolling is similar to that obtained by wire drawing. After 92% cold rolling of 1.0 mass% C steel, the tensile strength over 2500 MPa was achieved.

(cf. *ISIJ Int.*, **40** (2000), 1149)

Microstructural evolution of a 12Cr-2W-Cu-V-Nb steel during three-year service exposure

K. MIYATA et al.

Microstructural evolution of 12Cr-2W-Cu-V-Nb steel tubes (ASME SA213-T122) after one-year and three-year service exposure tests in a Japanese practical boiler has been investigated from a standpoint of the phase stability of precipitates. The test tubes consist of tempered martensite and δ -ferrite, and the main precipitates are MX-type carbonitride, $M_{23}C_6$ carbide and Laves phase. TEM observations on thin films show that the MX has precipitated in a plate-shaped with a coherent or semi-coherent relationship with the matrix inside grains. An estima-

tion of the lattice misfit between MX and the matrix suggests that the coherent strain has been high enough to enhance the shear stress and then strongly interact with dislocations. Another important point is that morphology and compositions of MX have been stable under the present service conditions, thereby the creep strength as well as tensile strength has kept high after long-term service exposure.

The long-term exposure to the present service temperature has enhanced the precipitation of $Fe_2(W, Mo)$ Laves phase inside grains, resulting in a marked reduction in the dissolved W and Mo in matrix. It is found that the kinetics of W-partitioning between matrix and Laves phase can be successfully expressed by the Johnson-Mehl-Avrami type equation and applied to estimate the actual temperatures of the exposed tubes.

It is concluded that the kinetics of Laves phase precipitation and morphology of MX have mainly controlled a microstructural stability in the 12Cr-2W-Cu-V-Nb steel, and also give helpful suggestion to increase the creep resistance during the long-term service exposure.

(cf. *ISIJ Int.*, **40** (2000), 1156)

Mechanical Properties

The effects of alloying elements on thermal fatigue and thermal shock resistance of the HSLA cast steels

J.H. PARK et al.

The effects of alloying elements on thermal properties of the HSLA (High Strength Low Alloy) cast steels have been investigated by thermal fatigue, thermal shock, and tensile tests. The thermal fatigue resistances of the HSLA cast steels were superior to those of SC42 cast steels. Excellent thermal resistances of the HSLA cast steels were mainly caused by high thermal conductivity, elastic modulus and tensile strength. In case of the HSLA cast steels, the steels with both Nb and V had more excellent thermal fatigue life than those with Nb or V individually. Increment of C contents gave a harmful effect on thermal fatigue resistance. In case of Mn contents,

HSLA cast steels with 1.2% Mn content had the highest thermal fatigue life among them and that with 1.5% Mn had lower thermal fatigue life than that with 1.2% Mn content. This result was attributed to rapidly increased bainitic acicular structure obtained by high Mn contents. Therefore, the optimum composition of HSLA cast steels to obtain the highest thermal fatigue resistance was 0.1%C-1.2%Mn-0.05%Nb-0.05%V, resulting in polygonal ferrite plus small amounts of bainitic microstructure. Thermal shock resistance of HSLA cast steels was also superior to that of SC42 cast steels. However, the difference between the HSLA cast steels with both Nb and V, and those with Nb or V individually has not been found.

(cf. *ISIJ Int.*, **40** (2000), 1164)

Micromechanical modeling of ferrite-pearlite steels using finite element unit cell models

N. ISHIKAWA et al.

An axisymmetric unit cell model based on a regular array of second-phase particles arranged on a BCC lattice is used to study deformation mechanisms of ferrite-pearlite structural steels. Microstructural characteristics of the steels were parameterized by the pearlite volume fraction, the aspect ratio of the pearlite particles, and the neighboring factor, which represents the ratio of interparticle spacing in the longitudinal direction to that in the transverse direction. FE analyses were carried out to investigate the macroscopic and microscopic response of unit cells with morphological features based on idealizations of the microstructures of the actual steels. Tensile properties of each constituent phase were obtained experimentally and used in the analyses. As compared to traditional axisymmetric models, the BCC cell model appears to be able to capture more realistically the behavior of the materials, and it accurately estimates the tensile behavior of the ferrite-pearlite steels even with a relatively large volume fraction of the pearlite phase. The effects of volume fraction and morphology of the second-phase particles on deformation behavior were also investigated.

(cf. *ISIJ Int.*, **40** (2000), 1170)