（＊掲載記事題目及び掲載頁は変更になる場合があります。）

Fundamentals of High Temperature Processes

Removal of Zn and Pb from Fe_2O_3–$ZnFe_2O_4$–ZnO–PbO mixture by selective chlorination and evaporation reactions

H.MATSUURA et al.

Selective chlorination and evaporation reactions could become one of the useful methods for the treatment of steelmaking dust containing zinc and lead. In the present study, chlorination rate of Fe_2O_3–$ZnFe_2O_4$–ZnO–PbO mixture with Ar–Cl_2–O_2 gas ($P_{Cl_2}=0.5\times10^4$ to 2.0×10^4 Pa, $P_{O_2}=1.0\times10^4$ to 5.1×10^4 Pa) has been measured at 1 073 K by gravimetry and the effects of partial pressures of chlorine and oxygen on the chlorination and evaporation rates have been investigated. Zinc oxide and lead oxide contained in the oxide mixture were selectively chlorinated and zinc and lead chlorides evaporated to gas phase, while iron oxide remained as oxide in a chlorinated residue. By chlorinating with Ar–Cl_2 gas, over 99% of zinc and lead could be removed from oxide mixture and approximately 3% of iron has been lost by chlorination and evaporation reactions simultaneously. To decrease the loss of iron oxide and improve the efficiency of selective chlorination and evaporation reactions, chlorination by using Ar–Cl_2–O_2 gas has been conducted and the enrichment of oxygen gas effectively depressed the chlorination of iron oxide, while the removal efficiency of zinc and lead was maintained.

(cf. *ISIJ Int.*, **46** (2006), 1113)

A process model for the carbothermic reduction of MnO from high carbon ferromanganese slag—The model

J.SAFARIAN et al.

In the present investigation, novel process modelling techniques have been applied to capture the kinetics of the MnO reduction process. The judicious construction of the constitutive equations makes full use of both dimensionless parameters and calibration methods to eliminate poorly known kinetic constants. The effects of different metallurgical parameters on the reaction kinetics are adequately captured by the model. Moreover, by invoking the concept of an isokinetic reaction, it has been possible to derive solutions where the temperature dependence of the process is uniquely described by the Scheil integral. The model is validated by comparison with experimental data, which following calibration yields an adequate predictive power. The applicability is illustrated in different numerical examples and its relevance will be further documented and explored in another paper.

(cf. *ISIJ Int.*, **46** (2006), 1120)

Kinetics of isothermal reduction of MgO with Al

J.YANG et al.

Isothermal reduction of magnesium oxide with aluminum was carried out by use of an insertion tube charged with pellets composed of magnesium oxide and aluminum powders. Since the temperature in the tube increased rapidly during inserting the tube into a high temperature zone in the graphite crucible and decreased quickly during lifting up the tube to a low temperature zone, the isothermal reduction condition was essentially satisfied by the present method.

The reduction rate was increased with increasing temperature, carrier gas flow rate and pellet forming pressure. Even a little carrier gas could greatly increase the reduction rate of magnesium oxide.

The 'XRD' patterns of pellets at different reduction stages confirmed that the aluminothermic reduction of magnesium oxide can be roughly classified into two stages. At the first stage, spinel, alumina and magnesium vapor were mainly produced; at the second stage, the spinel was further reduced by aluminum to produce alumina and magnesium vapor and the excessively added magnesium oxide was also reduced.

A kinetic model is established to describe the reduction rate of magnesium oxide. The apparent rate constant in the kinetic model increases with increasing temperature, carrier gas flow rate and pellet forming pressure. The apparent activation energy of the reduction is determined to be 109 kJ/mol.

(cf. *ISIJ Int.*, **46** (2006), 1130)

Fluid flow in a combined top and bottom blown reactor

M.ERSSON et al.

Physical modeling was done to study the flow field in a cylindrical bath agitated by bottom purging, top lance blowing and a combination of both injection types. A particle image velocimetry (PIV) system has been used to capture the velocity field of all three cases mentioned above. Special attention was paid to the recirculation loop. Top blowing creates a re-circulation loop in a relatively small volume close to the surface, compared to bottom- and combined-blowing. Increasing bottom flow rate moves the center of the re-circulation loop downwards into the liquid. When top blowing is combined with bottom blowing the center of the re-circulation loop is moved downwards into the liquid with increasing top lance flow rate.

(cf. *ISIJ Int.*, **46** (2006), 1137)

Correlation of flow establishment time for uniform dispersion of fine particles in a bath with an immersion cylinder

Y.TAKAHASHI et al.

Dispersion of fine particles in a hot metal bath is of essential importance for effective desulfurization and dephosphorization. Previous water model experiments revealed that rapid and uniform dispersion of fine particles in a mechanically agitated water bath can be achieved by immersing a circular cylinder slightly into the bath from its surface. Further water model experiments have been carried out in this study to derive an empirical equation for the period required for the uniform dispersion. This period is named the flow establishment time. Three types of impellers are chosen to take into account the effects of the shape and size of impeller on the flow establishment time.

(cf. *ISIJ Int.*, **46** (2006), 1143)

Studies on decarburisation and desiliconisation of levitated Fe–C–Si alloy droplets

D.WIDLUND et al.

The rate of decarburization and desiliconisation has been studied in several Fe–C–Si alloys containing 4% C and 0.37–0.71% Si using electromagnetically levitated droplets at 1 400 and 1 660°C in oxygen and helium atmospheres containing 10 and 20% oxygen. It has been found that the decarburization proceeds till a carbon content of about 0.5% is reached at a constant rate (the rates are 0.11 and 0.17%/s respectively for 10 and 20% oxygen) that is independent of temperature and silicon content. Beyond this carbon level, not only the decarburization rate has decreased but also the silicon content has started falling down. Optical microscopy studies showed typical white iron structures in the initial stages of decarburization (due to the small size of the droplet as well as rapid cooling) while low carbon acicular ferrite structure when $\%O_2$ was 20% and medium carbon structure when $\%O_2$ was 10%. This corresponded to the higher carbon content (~0.38%) of the latter. SEM studies did not reveal any oxide layer on the surface but EDS showed that the oxygen concentration was higher (0.02 to 0.24%) that extended to about 0.5 to 1 μm depth suggesting that oxygen gradients do occur even in the initial stages of decarburization due to the high level of turbulence within the droplet due to the electromagnetic effects in levitation. Calculations based on Thermocalc gave logarithmic decrease for decarburisation while it was found to be linear experimentally. This could be due to operating parameters other than diffusion (like convection) taking place or nonequilibrium conditions (created due to turbulence) and shorter times used for levitation.

(cf. *ISIJ Int.*, **46** (2006), 1149)

Ironmaking

Multi-phase flow simulations in direct iron ore smelting reduction process

H.-C.CHUANG et al.

The purpose of this study is to develop a computer simulation system to analyze the multi-phase (gas–liquid–slag) flow phenomena in the direct iron ore smelting reduction vessel to evaluate the conditions of stirring and mixing induced by bottom gas-blowing.

A computational fluid dynamics technique, called the SOLA-VOF method, has been used to treat the flow behavior of molten iron with free surface. As to the issue of the multi-phase, the Langrange and the Quasi-Single Phase concept were applied to analyze the flow behavior of injected gas, molten iron, and slag. The simulation system can be directly applied to analyze stirring processes at high flow rate gas and its related turbulent free surface.

The developed system was then applied to analyze the flow behavior in the 60% Experimental Smelting Reduction Vessel (ESRV). Interactions between injected gas and liquid bath, agitation of slag and mixing conditions of liquid bath and slag under different gas flow rates, bubble sizes, and arrangements of bottom-blown tuyeres were evaluated in

this study. The simulation results were then compared with water model experiments under similar flow conditions and were found to closely correspond with the experimental results.

(cf. *ISIJ Int.*, **46** (2006), 1158)

Characterization of thermal annealing effects on the evolution of coke carbon structure using Raman spectroscopy and X-ray diffraction

M.KAWAKAMI et al.

An experimental study was conducted to monitor the evolution of coke carbon structure during thermal annealing in a temperature range from 1 273 to 2 473 K in a bench-scale reactor. Coke carbon structure was characterized by using Raman Spectroscopy and the X-ray Diffraction. The Raman spectra of most of the cokes displayed two broad peaks G* (1 620 cm^{-1}) and D* (1 360 cm^{-1}). Both Raman peaks were deconvoluted into five peaks namely G, D, D′, R_1 and R_2. On the basis of area under the respective band peaks, new structural parameters were obtained to quantify graphitic (G), graphitic defect (D) and random (R) carbon fractions of cokes.

XRD analysis was used to show that stack height carbon crystallite, Lc, of coke increases with increasing annealing temperature while the impact of annealing duration was not significant particularly up to 1 873 K. On the other hand, average carbon crystallite width, La, did not improve significantly up to 1 873 K, and increased rapidly after subsequent rise in the annealing temperature. It appears that during annealing up to 1 873 K, modification of coke carbon structure could occur due to loss of basal carbon as a consequence of *in-situ* gasification.

The lateral expansion of carbon crystallite, La, was related to relative intensity or shape of Raman band peaks such that both parameters did not change significantly up to an annealing temperature of 1 873 K. At higher annealing temperatures, La values of coke increased with decreasing D/G ratio. Lateral expansion of carbon crystallite was attributed to progressive reduction of defects of graphitic carbon of coke, which can be monitored by D fraction of Raman Analysis. Combined Raman and XRD analysis suggested that rapid graphitization of coke may not occur along all dimensions until the annealing temperature exceeds 1 873 K.

Combining XRD and Raman analysis would provide a comprehensive evaluation of the evolution of coke carbon structure at different temperatures and their subsequent implications on the efficiency of various ironmaking operations.

(cf. *ISIJ Int.*, **46** (2006), 1165)

Steelmaking

Evaluation of bottom stirring system in BOF steelmaking vessel using cold model study and thermodynamic analysis

S.K.CHOUDHARY et al.

Water model experiments have been carried out in a 1/6th scaled down model of the basic oxygen steelmaking (BOF) converter in order to optimize the bottom tuyere configuration of a new vessel bottom. The mixing time in the model was determined by conductivity measurement technique for ten different types of bottom tuyere configurations. Amongst the various bottom tuyere configurations, the one consisting of 8 tuyeres in a symmetric non-equiangular position was found to be the best with respect to mixing in the vessel. The same bottom tuyere configuration of the new vessel bottom was compared with the previous bottom tuyere configuration (6 tuyeres), and about 40% improvement in the mixing in the bath was observed with the new bottom tuyere configuration. After determining the best bottom tuyere configuration from water model, it was implemented in the actual steelmaking vessel at the LD1 shop of Tata Steel. Average phosphorus partition ratio improved by 10 to 12 points, and the average $\%Fe_{total}$ in the slag dropped by about 1–2%, and a record vessel life of more than 2 000 heats was achieved in the first campaign itself with the new bottom tuyere configuration. Thermodynamic evaluation of dephosphorization in the BOF for different bottom stirring systems adopted by Tata Steel over a period of several years has been carried out using plant data of several heats. Gradual improvement in the approach to equilibrium due to improvement in the bottom stirring systems has been observed.

(cf. *ISIJ Int.*, **46** (2006), 1171)

A new method of removing inclusions in molten steel by injecting gas from the shroud

Q.Y.ZHANG et al.

A technology of removing inclusions in molten steel by injecting gas from the shroud has been analyzed and studied by method of mathematical model and water model. Study of position of injecting gas, flow rate of gas and gas nozzle size on the generated bubble size and distribution at the shroud has been investigated; the relationship between blowing parameters and inclusion removal efficiency has been analyzed in order to optimize the blowing parameters. The results show that the stronger turbulent vortex at the enlarged part in the shroud favors fine bubbles generation and uniform distribution; fine bubbles in diameter of 0.3 to 0.5 mm can be generated in the shroud and tundish by controlling flow rate of gas. The superfluous gas makes bubble size largen sharply. The nozzle size has some effect on bubbles size and distribution; the larger nozzle size goes against fine bubbles generation. So the optimum gas injected position is located at the enlarged part in the shroud. The resonable flow rate of gas and nozzle size would greatly improve inclusion removal efficiency.

(cf. *ISIJ Int.*, **46** (2006), 1177)

Casting and Solidification

Transient internal flow characterization of a bifurcated submerged entry nozzle

C.REAL et al.

Many authors have pointed out that the steel superficial quality strongly depends on the operating conditions at the continuous caster mold. The analysis of the dynamic behavior of the fluid inside the mold Submerged Entry Nozzle (SEN) was done in this work by means of numerical simulations. In this work, the tundish sliding nozzle was not included. The results of two different turbulence models, the K–ε and the Large Eddy Simulations (LES) models were compared. In simulations with both models, the velocity magnitude at 24 points inside the SEN was recorded every 0.001 s. The power spectrum of the results obtained with the LES turbulence model shows that the behavior inside the SEN is periodic. This behavior is compared with that obtained in physical simulations.

(cf. *ISIJ Int.*, **46** (2006), 1183)

Forming Processing and Thermomechanical Treatment

An investigation of different strategies for thermo-mechanical rolling of structural steel heavy plates

M.JONSSON

A software has been developed to determine optimal rolling passes in thermo-mechanical (TM) rolling in order to obtain a fine microstructure. It includes models of the effect of strain, precipitates, static and dynamic recrystallization and austenite grain size on the final grain size. It was also used to study the effect of different long interpass times during thermo-mechanical rolling of heavy plates. The predicted grain sizes for four different cases were compared with experimental results.

(cf. *ISIJ Int.*, **46** (2006), 1192)

Welding and Joining

Microstructures and mechanical properties of tungsten inert gas welded magnesium alloy AZ91D joints

D.Q.SUN et al.

Effects of weld composition and heat input on microstructures and mechanical properties of tungsten inert gas (TIG) welded magnesium alloy AZ91D joints have been investigated. Increasing magnesium alloy weld Al contents from 6.9 to 9.8 wt%, the area fraction of brittle $Al_{12}Mg_{17}$ phases in the weld metals increased from 6.2 to 7.3% and the strength and elongation of the weld metals decreased from 215 MPa and 7.9% to 192 MPa and 4.9%. Increasing the heat inputs from 73.6 to 147.2 kJ resulted in the grain coarsening of the weld metals and the partially melted zone (PMZ) width increasing from 120 to 210 μm. The mechanical properties of welded joints are poor compared with those of the base metal AZ91D. The strength and elongation of the joints are about 70% and 73% of the strength (156 MPa) and elongation (4.8%) of the base metal, respectively. The joint fractures mainly occurred in the PMZ with broader $Al_{12}Mg_{17}$ phases at the grain boundaries.

(cf. *ISIJ Int.*, **46** (2006), 1200)

Surface Treatment and Corrosion

Structure and polarization properties of Zn–Nb films formed on steel sheet by sputtering

H.KUBOYAMA et al.

Zn–Nb films were formed on a steel sheet by heli-

con plasma sputtering in an argon gas atmosphere at 1.0 Pa, at RF power of 50 W and DC power of 50 mA. The structure and polarization properties of these films were studied using EPMA, X-ray diffraction and polarization curve measurements. Zn plate-like crystals in Zn–Nb films decreased with increasing Nb content, resulting in a smooth surface over the entire film at Nb content of 30 mass% and above. The preferred orientation plane of Zn plate-like crystals was (0002) at 0 mass% Nb, while the orientation indices of $(10\bar{1}1)$ and $(10\bar{1}0)$Zn increased with rising Nb content. At 30–60 mass% Nb, the X-ray diffraction spectra showed a halo pattern characteristic of an amorphous structure. The corrosion current of Zn–Nb films, which was determined by polarization curves in 3% NaCl solution, decreased with increasing Nb content to reach a minimum value at 30–60 mass% Nb, corresponding to an amorphous structure.

(cf. *ISIJ Int.*, **46** (2006), 1205)

Atomic-scale structure of ferric oxyhydroxide formed from Fe–Si alloy in aqueous solutions containing different salts

S.-K.KWON et al.

Quantitative X-ray structural analysis coupled with reverse Monte Carlo (RMC) simulation was performed for characterizing the atomic-scale structure of γ-FeOOH (lepidocrocite) particles. These particles were formed by dipping pure iron or Fe–2mass%Si alloy into aqueous solutions containing Na_2SO_4 or NaCl. The realistic atomic-scale structures of γ-FeOOH particles were estimated by fitting ordinary interference functions through the RMC simulation technique. The results revealed that the fundamental FeO_6 octahedral structural units and their linkages were distorted in the γ-FeOOH particles formed from the Fe–Si alloy. This distortion was considered to be caused by the incorporation of silicate species into these particles. Transmission electron microscopy and Fourier-transform infrared (FT-IR) spectroscopy were employed for observing the morphology of the particles and for characterizing their bonding structure, respectively. Further, the amount of γ-FeOOH particles formed was measured in order to investigate their formation processes. The changes in the pH and oxidation-reduction potential (ORP) of the solutions were monitored during the formation of γ-FeOOH particles. Inductively coupled plasma analyses were also performed for determining the amounts of iron and silicon in supernatant solutions. The results indicated that the formation process of γ-FeOOH particles in the solutions was influenced by the addition of silicon to iron.

(cf. *ISIJ Int.*, **46** (2006), 1210)

Initial stage of localized corrosion in artificial pits formed with photon rupture on 55mass%Al–Zn coated steels

M.SAKAIRI et al.

The photon rupture method, whose oxide film and metal are removed by focused pulsed Nd–YAG laser beam irradiation was applied to form artificial micro pits in 55 mass% aluminum–zinc coated steels. The 15 μm coated layer was removed by 2 s of continuous laser irradiation in this experiment. The rest potential transients were measured during the laser irradiation. While the coated layer covered the steel substrate, the rest potential change in the negative direction just after the starts of the laser irradiation and then returned to the previous value. However, after the steel substrate was exposed to solution, the rest potential moved in the positive direction immediately after the discontinuation of the laser irradiation and then also returned to the previous value. The amplitude and duration of the potential changes after the laser irradiation increased with longer irradiation, related to the pit depth and exposed area ratio of coated layer/steel substrate. These rest potential fluctuation differences can be explained by galvanic reaction changes in the artificial pit formed on the coated steel during irradiation.

(cf. *ISIJ Int.*, **46** (2006), 1218)

Transformations and Microstructures

Laser-ultrasonic monitoring of austenite recrystallization in C–Mn steel

A.SMITH et al.

The static recrystallization kinetics of hot deformed austenite were characterised by a combination of *in-situ* laser-ultrasonics and stress relaxation measurements. Samples were deformed in compression at temperatures of 850°C and 900°C. The applied strain was varied between 0.2 and 0.5, whilst the strain rates used were $0.1\,s^{-1}$ and $0.5\,s^{-1}$. At various points during annealing samples were quenched and analysed by optical microscopy.

During recovery prior to recrystallization the ultrasonic velocity change and attenuation were almost constant. During recrystallization, the velocity change and attenuation decreased for the conditions imposed. The decrease in velocity change was mostly due to a change in the overall texture. The decrease in attenuation could be explained by a change in grain size. Unfortunately, the additional effect of dislocation damping on attenuation could not be quantified.

Comparison of the stress relaxation kinetics with the observed decrease in ultrasonic velocity change and attenuation generally showed good agreement.

From the attenuation measurements the grain sizes in the recrystallised structure for various applied strains were calculated. Comparison with grain sizes determined from optical microscopy, showed reasonable agreement considering the accuracy of the attenuation measurements and the assumptions made.

(cf. *ISIJ Int.*, **46** (2006), 1223)

Particle-stimulated nucleation of ferrite in heavy steel sections

K.F.A.HAJERI et al.

In heavy steel sections, strength and toughness are improved remarkably by refining and homogenizing the final ferrite microstructure. The production of heavy sections by universal-type rolling mills takes place at elevated temperature followed by slow cooling rates. Therefore, refinement of the ferrite microstructure through modern thermomechanical, TMP, techniques is not feasible. This paper explores and presents the use of particle-stimulated nucleation of ferrite, the PSN (particle-stimulated nucleation) mechanism, to refine the ferrite grain size and eliminate the high-carbon, low transformation products otherwise found in transformed coarse-grained austenite. In this study, MnS and Ti-oxide particles were used to promote intragranular ferrite, or IGF, in a typical ASTM A572 grade 50 Steel. This work included the study of the decomposition behavior of coarse grained austenite as a function of very slow cooling rate. In addition, the nucleation of ferrite grains taking place at γ/γ, γ/α and γ/inclusion interfaces was identified and quantified.

(cf. *ISIJ Int.*, **46** (2006), 1233)

Mechanical Properties

Acoustic emission technique to study the effect of strain rate on the deformation behaviour of TRIP aided steels with different matrix microstructures

M.MUKHERJEE et al.

Acoustic Emission (AE) signals generated during the tensile deformation of three TRIP-aided steels with different matrix microstructures were monitored. The tensile tests were carried out at four different strain rates varying from 3.33×10^{-5} to $3.33\times10^{-2}\,s-1$ and additional intermittent tests were carried out at the lowest and highest strain rates to estimate the extent of deformation induced austenite to martensite transformation using X-ray diffraction analysis. Good correlation was obtained between AE and X-ray diffraction analyses. Both techniques showed that increasing strain rate restricted progressive transformation of retained austenite to martensite. The energy of continuous AE signals generated during tensile test conducted at high strain rate ($3.33\times10^{-2}\,s-1$) was found to be directly proportional to the fraction of martensite formed. The proportionality constant (k) was influenced by the matrix microstructure; steels with polygonal ferrite matrix manifesting a higher k value than steels with annealed martensite matrix or bainitic ferrite matrix.

(cf. *ISIJ Int.*, **46** (2006), 1241)

Effect of the addition of P on the mechanical properties of low alloyed TRIP steels

L.BARBÉ et al.

Common TRIP (TRansformation Induced Plasticity)-aided steels contain roughly 0.15 mass% C, 1.5 mass% Si and 1.5 mass% Mn. The high Si contents in conventional CMnSi TRIP-aided steels are known to cause low ductility levels in the as-cast condition and give rise to galvanizing problems which is an essential challenge limiting their use in automotive applications. Partial substitution of the Si by Al leads to improved galvanising properties, but a loss in strength. The effects of substituting the Si and Al partially by P was therefore studied in detail with a special attention to the processing conditions in the hot dip galvanizing and continuous annealing processes. The addition of P was found to result in a higher amount of retained austenite which

was more resistant to decomposition at longer austempering times compared to non-P alloyed TRIP steel. A synergetic effect of Si and P was observed as the increase in tensile strength per mass% Si was five times larger than expected for solid solution strengthening. The volume fraction of retained austenite was found to depend very much on the annealing cycle, with long austempering times resulting in lower amounts of retained austenite (6 to 12 vol%), while short austempering times resulted in higher retained austenite contents (12 to 20 vol%).

(cf. *ISIJ Int.*, **46** (2006), 1251)

Physical Properties

Stress relaxation behavior of molten slags

T.MATSUSHITA et al.

In the present work, a method to measure stress relaxation of molten slags, developed earlier by one of the authors, was applied to mould flux slags as well as synthetic slags. The molten slag was sandwiched by two Pt plates and was compressed. And stress relaxation tests (the structural relaxation of molten slags) have been conducted by compressing the molten slags as well as mould flux slags at strain rates of 10 mm/min. The results of stress relaxation tests were discussed from the viewpoint of relaxation time and structure of slags with the aid of Raman spectroscopy. The stress relaxation behavior is found to be linked to the structure of slags. The residual stress after a compression was increased with increasing of Al_2O_3 content and with decreasing of CaF_2 content. The relaxation behavior was changed drastically with increasing of temperature for some molten slags.

(cf. *ISIJ Int.*, **46** (2006), 1258)