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Process Developments of Iron and Steelmaking and Enviromental Challenges

Optimization of ironmaking process for reducing CO_2 emissions in the integrated steel works (Review)

T.ARIYAMA et al.

Global warming is a common subject in steel industry in every country. International cooperation will be required using the Kyoto Mechanism from global aspect. In the integrated steel works, there are various means to decrease reducing agent at blast furnace, however, preferable way to reduce CO_2 emissions must be chosen considering energy balance in whole steel works, and energy saving must be actively pursued. Injection of waste plastics and carbon neutral materials such as biomass is better alternative. In the near future, hydrogen will attract attention as a clean energy source even in the steel works. Regarding oxygen blast furnace and smelting reduction, the possibility of CO_2 reduction is dependent on optimum system design of total process including outside process. Charge of prereduced sinter and high reactivity coke to blast furnace leads to reduction of CO_2, keeping current blast furnace facility and capability.

(cf. *ISIJ Int.*, **46** (2006), 1736)

Dust injection in iron and steel metallurgy (Review)

D.SENK et al.

The occurrence of dusts in steelworks is surveyed. A brief overview of the European legislation situation is given. Current techniques of solid injection in different aggregates are presented. The investigations of the Department of Ferrous Metallurgy (IEHK) at RWTH Aachen University in the handling of various dusts in metallurgical processes are introduced. The dust injection into shaft furnaces and steel melts has been chosen as typical treatments. Former researches and recent works are presented and the results are discussed.

(cf. *ISIJ Int.*, **46** (2006), 1745)

Reduction of CO_2 emissions from integrated steelmaking by optimised scrap strategies: Application of process integration models on the BF–BOF system

C.RYMAN et al.

In integrated steelmaking there are a number of means to reduce CO_2 emissions. One approach is to increase the metallic Fe input to the production system. A common belief is that scrap works as a CO_2 diluent when introduced in iron ore based steelmaking. It is not necessarily so. Scrap is a key supplementary charge material in oxygen steelmaking converters, but scrap can also be utilised in ironmaking where it will decrease the use of reducing agents and with that also the specific CO_2 emissions. By the use of a process integration model which basically includes the primary processes of cokemaking, sintering, ironmaking and oxygen steelmaking the overall influence of scrap input on CO_2 emissions is demonstrated and commented. The influence of hot metal silicon content is elucidated by calculations with different material and process constraints. The results show that at moderate scrap rates, the reduction of CO_2 emissions is favoured by increased scrap additions to the oxygen converter. When the scrap additions to the converter balances the actual heat capacity of the bath, other means to achieve an increased scrap melting capacity can be taken into account. This include combinations of scrap addition to the blast furnace, increased silicon content in tapped hot metal, and/or addition of Ferro-silicon combined with further scrap additions to the oxygen converter. Different strategies for CO_2 emission reduction have to be suggested depending on if the objective is to minimise the site (direct) emissions or the global (indirect+direct) emissions.

(cf. *ISIJ Int.*, **46** (2006), 1752)

Analysis on material and energy balances of ironmaking systems on blast furnace operations with metallic charging, top gas recycling and natural gas injection

H.NOGAMI et al.

The iron and steelmaking industry has been receiving social pressure to reduce energy consumption and environmental load as recent increase in the social awareness on environmental and resource problems. The ironmaking system consumes more than a half of overall energy input to the steelwork and its improvement is expected as a countermeasure for such problems. Numerous attempts through improving the blast furnace operation have been made. This paper analyzes material and energy balances of ironmaking system that consists of hot stove, coke oven, CDQ, sintering and blast furnace. The operation statuses of the blast furnace with natural gas injection, metallic charging and top gas recycling that have been obtained by the kinetic-based numerical simulations are applied to this analysis. The results suggested that the metallic charging to blast furnace decreases both energy input and CO_2 emission. The natural gas injection operation decreases the CO_2 emission from the iron making system while the decrease in the energy input is small. The top gas recycling operation increases the CO_2 emission due to the scrubbed CO_2 from the recycled top gas.

(cf. *ISIJ Int.*, **46** (2006), 1759)

Results and trends on the injection of plastics and ASR into the blast furnace

J.BUCHWALDER et al.

As an alternative to the injection of oil or pulverized coal, the injection of waste plastics is common operational practice in a number of blast furnaces. Over and above that the trend of using other waste materials as auxiliary reducing agents should also be noted. The injection of ASR has also been tested, but has not yet been introduced into normal operational conditions. From the metallurgical point of view it could be advantageous to inject synthesis gas made from ASR instead of the injection of granulated ASR itself. Such a synthesis gas could be injected into the tuyeres at the raceway level, as well as into additional tuyeres at the lower part of the shaft. Simulation model calculations promise considerable savings in coke consumption with higher productivity with shaft gas injection.

(cf. *ISIJ Int.*, **46** (2006), 1767)

Advanced process modelling of hot metal desulphurisation by injection of Mg and CaO

H.-J.VISSER et al.

To improve the lime–magnesium desulphurisation process at BOS No. 2 at Corus Strip Products IJmuiden, a process model is derived based on the description for the bubble plume generated by injected carrier gas and reaction kinetics of the desulphurisation agents. The model is suited to simulate variations of gas flow and injection rates of CaO and Mg during the process. A parameter study was done in order to improve the operational practice. To validate the model assumptions and to get more knowledge of the reactions of Mg, hot metal samples have been taken before, during and after desulphurisation. SEM analysis revealed (Mg, Mn)S particles with varying Mn content, often combined with Ti(C, N) accumulated in the hot metal. The morphology of the interface between slag and steel has been studied.

(cf. *ISIJ Int.*, **46** (2006), 1771)

The effect of magnesium gas injecting conditions on the rate of hot metal desulfurization

S.MUKAWA et al.

Possibility of high efficiency desulfurization of hot metal by magnesium gas was suggested from 350 g scale experiments in previous reports.[1–4] The present study proves the possibility on the basis of 30 kg scale experiments. Conbination of dilution of magnesium gas by argon gas and use of the injector which has 6 narrow exit holes allows to obtain magnesium efficiency of 74% at a quantity of magnesium of 0.2 kg per ton hot metal at the initial sulfur content of 0.02 mass%.

(cf. *ISIJ Int.*, **46** (2006), 1778)

Behavior of ironmaking slag permeation to carbonaceous material layer

K.SAITO et al.

To investigate the slag permeation to packed bed of carbonaceous materials, the measurement of molten slag's densities, surface tensions and dynamic contact angle on carbonaceous materials at relatively low temperatures (from 1 673 to 1 773 K) are carried out by applying the sessile droplet method. The interfacial compositions of slags and carbonaceous materials were examined by SEM/EDX. SiC at carbonaceous material surface was not observed. The variation of measured density, contact angle and surface tension with time were found to be almost negligible with given slag composition and at given temperature. It is reported that carbonaceous material wettability at the temperature of more than 1 873 K was strongly dependent on the slag composition as well as carbon properties. The almost constant contact angel with time in this study can be attributed to the negligible formation of SiC at carbonaceous material surface.

The slag permeation model has been developed along with the measurement of physical properties. The maximum retention height of liquid layer on the sphere packing layer is expressed by $H_C=A/L_C+L_C/2$, where A is constant and H_C and L_C are the dimensionless slag layer retention height and the dimensionless sphere's diameter, respectively. Slag layer retention height on the carbonaceous material packing layer is evaluated using the measured physical properties. The proposed characteristic length $\lambda(=\sqrt{-\gamma_L \cos\theta/\rho g})$ in the model can be used to characterize the slag permeation behaviour.

(cf. *ISIJ Int.*, **46** (2006), 1783)

The evaluation of the mixing properties of the mechanically stirred cylindrical vessel

K.ITO et al.

The effect of baffles on the mixing of bath liquid and solid particles was investigated using a water model for the mechanically stirred vessel. The baffle whose width is 1/10 of the vessel diameter was enough to enhance the liquid-particles mixing. The LDV measurement showed the formation of the unsteady vertical flow by the baffle. The concept of information entropy was introduced for the evaluation of the mixing properties of the reactor. The vessel was divided into 35 regions and the transition probability for each region was estimated from the velocity profiles obtained from the LDV measurement. The complete mixing time was predicted by the calculation and compared with the observations.

(cf. *ISIJ Int.*, **46** (2006), 1791)

Technology for production of austenite type clean stainless steel

K.SAKATA

We established the refining technology for cleanliness in regard to austenite type stainless steel. But immersion nozzle clogging in continuous casting occurred by formation of spinel ($MgO–Al_2O_3$) type inclusions in strong reduction refining for cleanliness. Therefore, we estimated the conditions for formation of spinel and it was possible to improve the castability while keeping cleanliness by controlling of inclusion compositions.

(cf. *ISIJ Int.*, **46** (2006), 1795)

Forming Processing and Thermomechanical Treatment

Recent topics of research and development in continuous casting (Review)

T.MATSUMIYA

Three major issues in continuous casting are nonmetallic inclusions, cracking and segregation. By the application of electromagnetic stirring (EMS) in mold the inclusion entrapment by the growing initial solid shell is hindered and the number of inclusions near the surface of slabs is much reduced. By the application of level magnetic field (LMF) the downward liquid flow induced by the exit flow from submerged entry nozzle is much decelerated and the entrapment of large size inclusions inside the slabs is eliminated, which otherwise cause inner defects. Electromagnetic casting (EMC) prevents from the formation of oscillation mark and hook mark, concomitantly eliminates the entrapment of inclusions and bubbles at the hook mark and also prevents from the formation of surface depression and longitudinal surface cracking in hypo-peritectic steels. Resonance-like unsteady bulging with oscillation of molten metal level in mold causes internal cracking and can be prevented by unequally spaced support rolls. Macrosegregation can be reduced by the proper reduction of casting thickness or, in the case of bloom, the minimization of the size of equiaxed solids, which can be realized by the application of EMS.

(cf. *ISIJ Int.*, **46** (2006), 1800)

Effect of Na_2O on crystallization of mould fluxes for continuous casting of steel (Review)

M.HAYASHI et al.

The effect of Na_2O on the behavior and mechanism of the precipitation of cuspidine from the $CaO–SiO_2–CaF_2–Na_2O$ quaternary slags has been investigated by solid-state ^{19}F nuclear magnetic resonance spectroscopy, differential thermal analysis and X-ray diffraction analysis. It is found that F^- predominantly bonds with Ca^{2+} rather than Na^+ in the composition range of the commercial mould fluxes. This result indicates that the presence of Na_2O may not prevent the precipitation of cuspidine from the slags. The glass transformation temperature and the crystallization temperature of cuspidine decrease with increasing Na_2O content. The mass fraction of cuspidine in the samples heated at 973 K was obtained as a function of heat treatment time. It is found that the mass fraction of cuspidine significantly increases at the early stage of the heat treatment, but levels off later on. The mass fraction of cuspidine at the leveling-off is the largest for the sample with 4 mass% Na_2O, and is smaller as the Na_2O content is either smaller or larger than 4 mass%. It is also found that the incubation period is observed before the crystallization starts, and that the incubation period is shorter as the Na_2O content in the sample is larger.

(cf. *ISIJ Int.*, **46** (2006), 1805)

Interfacial properties of molten low carbon steel containing Ti, Nb or B in relation to the behavior of fine particles in continuous casting process

K.MUKAI et al.

The surface tension of molten low-carbon (LC) steel containing Ti, Nb or B and the contact angle between the molten steel and solid alumina were measured using the sessile droplet method under an Ar gas atmosphere at 1 500°C, 1 575°C and 1 600°C. The results show that Ti decreases the surface tension of molten LC steel and the contact angle. The interfacial tension between molten LC steel containing Ti and solid alumina decreases with the increase in Ti content. The work of adhesion between molten LC steel and solid alumina decreases slightly at 1 550°C, but increases at 1 600°C with increasing Ti content. The addition of a small amount of Nb or B to molten LC steel decreases slightly the surface tension of the molten steel. The effect of Nb on the contact angle between molten LC steel and solid alumina is less, but B markedly decreases the contact angle when the B content increases from 0.0504 to 0.0999 mass%. It can be deduced that fine bubbles are more easily entrapped by the solidifying shell for LC steel with Ti or B than that with Nb, while fine alumina inclusions are more easily entrapped by the solidifying shell for LC steel with B than that with Ti or Nb.

(cf. *ISIJ Int.*, **46** (2006), 1810)

Influence of sulphur content and molten steel flow on entrapment of bubbles to solid/liquid interface

T.MIYAKE et al.

The sliver defects which occur easily on ultra low carbon steel sheet are the most harmful defects, especially to automobile outer panel products. There may be many causes of the sliver defects such as nonmetallic inclusions, bubbles, surface cracks and inner cracks. However, crack formation is not a serious problem in continuously cast ultra low carbon steel because of its good ductility at high temperatures. Therefore, it is important to reduce the amount of nonmetallic inclusions and bubbles just below the slab surface. Electro-Magnetic Stirring in the mold (M-EMS) is an effective tool to remove such bubbles and reduce the amount of the sliver defects, although the effects of M-EMS on the reduction in sliver defects are influenced by the chemical composition of steel, especially by the sulphur content. The slabs cast at No.4CC-1st strand in Kakogawa Works reveal rather a high content of bubbles when the sulphur content is higher and M-EMS is not applied. In this study, the reason why sliver defects caused by bubbles are more likely to occur on steel of higher sulphur content is discussed based on the interaction between advanced solid/liquid interface and bubbles. The forces acting on the bubbles are theoretically described as a function of bubble radius, velocity and interfacial tension gradient of liquid steel in front of a solid/liquid interface.

(cf. *ISIJ Int.*, **46** (2006), 1817)

A simple innovation in continuous casting mold technology for fluid flow and surface standing waves control

M.KAMAL et al.

This paper reports on the development of a novel technique to control standing surface waves and turbulence. The technique uses external refractory shapes in the continuous casting mold to modify fluid flow and control the surface waves. The method is both economical and flexible as compared to contemporary technologies to solve the problem. Two distinct methods are described based on the placement of the shapes in the mold. Type A shapes are placed nearer the free surface and predominantly work by modifying the upper recirculation region. Type B shapes are placed deeper in the mold and work by altering the overall fluid flow pattern. Water modeling was carried out on thin and thick slab caster models to understand the behavior of the surface waves. An optimum design of flow control device and its positioning were developed based on the study. Mathematical modeling using commercial fluid flow codes was also used to supplement the ex-

perimental results of the process.

(cf. *ISIJ Int.*, **46** (2006), 1823)

Effects of electromagnetic brake on vortex flows in thin slab continuous casting mold

B.LI et al.

A mathematical model has been developed to understand the vortex flows in the thin slab continuous casting mold associated with the effect of electromagnetic brake (EMBR). The molten steel flows are discharged from the bifurcated ports of the submerged entry nozzle (SEN) in the mold. Low Reynolds number k–ε turbulence model is used to calculate the effective viscosity. Numerical simulation shows that the asymmetric vortices can be produced even though the geometry is symmetrical and inlet flows are steady. Asymmetric flow is caused by the perturbation of numerical error of iteration in simulation instead of actual nozzle clogging, off-centerness of nozzle, and random turbulence *etc.* The vortex intensity depends on the surface velocity in the mold, which is determined by outflow angle of nozzle and casting speed. The vortices can be significantly suppressed and deformed by the application of static magnetic field, but cannot be vanished completely. The surface velocities decrease significantly with increasing coil currents, and the level of fluctuation heights in the mold becomes remarkably small. Furthermore, the aberration parts in adjacent to SEN caused by the vortices is gently calm. The vertical velocities in the lower part of the mold are suppressed and the plug like flows are formed.

(cf. *ISIJ Int.*, **46** (2006), 1833)

Principles of billet oft-reduction and consequences for continuous casting

R.THOME et al.

The production of continuously cast products that show very low center segregation and are thus more homogeneous is an important objective, particularly for high-speed continuous casting of billets, in meeting quality requirements that are becoming increasingly stringent. In addition to the well-known methods of reducing macro-segregation in continuous casting, inline thickness reduction of the partially solidified strand, already used successfully in slab and bloom casting, offers an alternative for producing material with low segregation level.

In the present report, which considers the feasibility and effectiveness of a mechanical soft-reduction for the continuous casting of billets, the influence of the soft-reduction position from the metallurgical point of view, the reduction parameter and the roll diameter in combination with the structural design of the soft-reduction unit was assessed comparatively. One strand of the billet caster S4 was modified for this purpose and soft-reduction trials were carried out on high carbon steel grade D72C for wire rod application and spring steel grade 54SiCr6 at casting speeds between 2.80 and 3.60 m/min. The conclusions drawn from the test results with respect to required solid fraction in the liquid core, effective reduction rate and necessary roll diameter formed the basis for designing the soft-reduction unit of billet caster S0 and for predicting favourable process parameters. First results of billet soft-reduction trials on the caster S0 are presented.

(cf. *ISIJ Int.*, **46** (2006), 1839)

Methods for assessment of slab centre segregation as a tool to control slab continuous casting with soft reduction

H.PREßLINGER et al.

Slabs produced by continuous casting are characterized by macrosegregation in their central regions. The formation of this macrosegregation depends on many parameters, among others the state of the casting line and the casting technique used.

In order to minimize this slab centre macrosegregation for the various steel grades, appropriate samples cut from the slabs have to be subjected to a quantitative assessment. Optical methods of assessment are too inaccurate to serve, for example, as a useful index for controlling soft reduction. For this reason the centre of the slab was analysed using several physical and chemical test methods whose results were then cross-compared. In the process, a combination of ultrasonic porosity tests and spark analyses (OES-PDA) turned out to be the most informative, cost-effective and fastest method for assessing macrosegregations.

Thanks to the macrosegregation indexes elaborated on the basis of the test results for the individual slabs it is now possible to find optimum casting parameters such as casting temperature, casting speed *etc.* for the subsequent melts of the same steel grade and also to use soft reduction for the purpose of minimizing macrosegregation phenomena.

(cf. *ISIJ Int.*, **46** (2006), 1845)

Semi-solid processing of alloys: Principles, thermodynamic selection criteria, applicability

B.HALLSTEDT et al.

Semi-solid processing (SSP) of alloys makes use of the thixotropic properties of two-phase mixtures of globulites and liquid. These materials whose viscosity decreases under shear deformation and increases again once the shear action ceases, can be handled almost like solids in the absence of shear stress and they can flow like viscous liquids when deformation forces are applied. SSP requires a wide melting interval of the alloy, a low temperature sensitivity of the phase fractions in the slurry and a tendency to form a fine-grained globulitic microstructure.

The numeric simulation of solidification has proven useful for the selection of alloys to be processed in the semi-solid state. To obtain results applicable in practice, the methods to be used depend on the alloy systems, reaching from equilibrium calculations and Scheil-Gulliver estimations to diffusion simulations. All simulations depend on reliable thermodynamic and kinetic databases. Instead of using only the slope of the fraction liquid curve at 50% liquid as selection criterion, we suggest to use the thixo ranges ΔT^{40-60} for thixocasting and ΔT^{20-40} for thixoforging. Using these selection criteria we investigated the suitability of three Al alloys and three steels including the influence of compositional variations.

So far, the industrial large-scale production of parts by SSP has been confined to aluminium alloys, although extensive development efforts are being made to apply the process to magnesium, to nickel alloys and to steels.

(cf. *ISIJ Int.*, **46** (2006), 1852)

Shape flow casting and in-rotating-liquid-spinning processes for the continuous production of wires and of high-strength and soft magnetic metallic fibres

G.FROMMEYER et al.

Computer-controlled facilities for continuous casting of metallic fibres and wires performing in-rotating-liquid spinning (INROLISP) and shape flow casting (SFC) were designed and installed to determine and control the near-net-shape casting processes over an extended production period. In particular, the flow behaviour of the melt jet was experimentally investigated and theoretically described using fluid dynamic equations. The controlling process parameters, such as the velocity of the melt jet, the stable free flight length, the nozzle geometry and cooling rate, were examined and optimised. Several pure metals as well as microcrystalline and amorphous alloys were cast into continuous fibres and wires of high quality. Microstructural features and mechanical properties of rapidly quenched fibres and thin wires were also evaluated. Of great potential application is the production of amorphous soft-magnetic Fe base and Co base thin wires with diameters of about 30 to 50 μm. These microwires are used as sensor cores in highly sensitive novel magnetic field sensors based on a magneto-electric effect. Direct casting of wires with diameters up to 3 mm is carried out using the shape flow casting technique. The SFC facility is an highly instrumented modified meltspin facility, performing rapid substrate quenching. The process principles of the SFC technology, which enable a flexible production of steel, nickel base alloy wires and other novel materials are presented. The microstructural features are correlated with the process parameters.

(cf. *ISIJ Int.*, **46** (2006), 1858)

Nb-alloyed Cr-steel in simulated strip casting process

P.R.SCHELLER et al.

Nb alloyed ferritic Cr-steel is usually produced by continuous casting with following hot and cold rolling procedure. In the laboratory scale the possible new route *via* strip casting was studied. The scope of the investigation in simulated process route was the development of microstructure and precipitations.

In the experiments process parameters similar to those of the real strip caster were chosen, then those of hot rolling and cold rolling of such cast strips. The quickly solidified layer was produced by immersion of a steel substrate under vacuum into melt. The microstructure showed small niobium precipitates in the grain matrix and at the grain boundaries. Their size and distribution was evaluated for different niobium contents and cooling rates in the as-solidified structure. The diffusion controlled change of

the precipitate morphology was also analysed after preheating and rolling. Reprecipitation and precipitate growth, as well as dissolution of precipitations at the grain boundaries were observed. The effect of various cooling rates and niobium content on the shape and formation of niobium containing precipitates and on the grain boundary is discussed.

Thermodynamic calculations using FactSage were carried out in order to predict the precipitation of Nb-rich phases in ferritic stainless steels. The effect of the chemical composition and temperature on the thermodynamic stability of these precipitates was evaluated.

(cf. *ISIJ Int.*, **46** (2006), 1865)

Effect of niobium on the formation of microstructure and grain boundary in Fe–Nb and Fe–C–Nb alloys

M.KUDOH et al.

The changes in degree of undercooling, secondary dendrite arm spacing and microstructure were investigated by using three cooling methods. The Fe–Nb binary alloys and Fe–0.1mass%C–Nb ternary alloys having various niobium concentrations ranging from 0.50 to 6 mass% were used. The Fe–C–Nb ternary alloys were used to investigate the role of niobiumcarbide (NbC) as the heterogeneous nucleation site. The degree of undercooling in both alloys changed with niobium concentration and that in the ternary alloy was always smaller than that in the binary alloys because of the presence of NbC. Dendritic microstructures were observed in both alloys quenched from 1 673 K after cooling at a rate of 0.028 K/s when Nb concentration exceeds 2 mass%. An Fe–0.1mass%C–3.0mass%Nb alloy air-cooled from 1 473 K also exhibited the dendritic microstructure, while an Fe–3.0%Nb alloy similarly air-cooled did not exhibit the dendritic microstructure. Then, grain boundary in the Fe–0.1mass%C–3.0mass%Nb alloy was formed between the arrays of dendrites, while it wasn't formed between secondary dendrite arms. Furthermore, the microstructure in an Fe–0.10%C–1.0%Nb alloy which was air-cooled from liquid state exhibited fine dendrite microstructure.

(cf. *ISIJ Int.*, **46** (2006), 1871)