（＊掲載記事題目及び掲載頁は変更になる場合があります。）

Gas evolution during mechanical milling of hematite–graphite mixture

Y.KASHIWAYA et al.

In previous studies, the reactivity of hematite–graphite mixture obtained by the mechanical milling was investigated. The rate of reaction has remarkably increased and the starting temperature of reaction decreased with the milling time. Understanding the phenomena and its mechanism occurring in the milling would contribute to develop the new feeding material for ironmaking process.

In this study, milling of hematite and graphite mixture was carried out with the same procedure. Gas analysis by QMS was performed to clarify the evolved gas during milling qualitatively and quantitatively.

Gas evolution from graphite was mainly CO gas. CO_2 gas also evolved in the early stage of milling. These gases would be related to the adsorbed gases before milling. When the sample exposed to air in the course of milling, much gas adsorbed on the surface of milled graphite, which increased with the increasing milling time.

When the hematite and graphite mixture was milled under argon atmosphere, mainly CO gas evolved owing to the reduction reaction.

From these results of gas analysis, the mechanisms for the gas evolution during the milling were proposed.

(cf. *ISIJ Int.*, **44** (2004), 1980)

Characteristics of nano-reactor and phenomena during mechanical milling of hematite–graphite mixture

Y.KASHIWAYA et al.

The mechanical milling of hematite and graphite mixture could accelerate the reaction rate extremely, when the mixture after milling was heated up under inert atmosphere. In the previous study, the authors have indicated not only the high reaction rate but also the low starting temperature of the reaction. These phenomena can be understood through the view point of the nano-reactor and the active complex. The nano-reactor was defined in this study through the observation of the milling products by TEM and FE-SEM. The important characteristic of nano-reactor was proposed.

Moreover, the phenomena such as the reduction reaction, the phase transformation(formation of an active complex) and the crystalline size degradation occurring in the course of the milling were examined. It was found that the milling of mixture gave a different phenomenon from the single hematite or graphite milling. Furthermore, the atmosphere during the milling affected on the reactivity of the milling product. The existence of oxygen caused the reoxidation of the reduction product which resulted in the different crystalline size after milling.

(cf. *ISIJ Int.*, **44** (2004), 1985)

Analysis of the transition state of the carbon and iron oxide mixture activated by mechanical milling

Y.KASHIWAYA et al.

In previous study, the extremely high reaction rate obtained by the mechanical milling has been reported. It was found that the phenomena were quite complicated and the many factors were affected on the reactivity. Among these factors, the crystal state of hematite and atmosphere (air and argon) during the milling were quite important ones.

Milling of hematite and graphite mixture was carried out both in the air and in the argon. Rate constants for the reactions were obtained by kinetic analysis. The enthalpy ΔH^* and entropy ΔS^* of activation were estimated on the basis of transition state theory. The interpretation of ΔS^* and ΔH^* was performed to explain the effect of milling on the reactivity related to the milling conditions.

The temperature of peak of reaction curve decreased with increasing milling time. The reactivity of the sample milled in the argon atmosphere showed higher reactivity than that milled in the air. The enthalpy ΔH^* and entropy ΔS^* of activation were obtained from experimental rate constants. The variation of ΔH^* and ΔS^* with milling time showed opposite tendency between the sample milled in the air and in the argon. It was considered that the active complex having loose bonding would form during milling in the air atmosphere. On the other hand, the active complex having a structure closed to the product (metallic iron) might form.

(cf. *ISIJ Int.*, **44** (2004), 1991)

Carburized carbon content of reduced iron and direct carburization in carbon composite iron ore pellets heated at elevated temperature

Y.IGUCHI et al.

Using coal char, coke and graphite, carbon composite iron ore pellets of 18 mm in diameter with the mixing ratio of [reducible oxygen mol(O)]/[fixed carbon mol(C)]=1 were prepared inside a rotating tire. The pellets were heated in nitrogen at 1 150–1 380°C until reactions just finished. The reacted pellet was separated into a shell part and a core part. The pulverized shell and core parts were repeatedly cleaned in ethanol under ultrasonic vibration to thoroughly remove attached carbon particles. The content of carbon dissolved in reduced iron was measured by analyzing them by the combustion method. The direct carburization through direct contact points is the major reaction and the gaseous carburization is the minor one. Coal char bearing pellets showed carbon contents much less than the others; less than 0.5% in shell and increased with temperature at last exceeding solidus line at 1 300°C in core. Increase in the mixing amount of char showed no change in the carbon content. But roughening the char significantly increased the content. Coke bearing pellets showed carbon contents near to solidus line in shell and between solidus and liquidus lines in core. Graphite bearing pellets showed carbon content almost agreed with solidus line in shell and above liquidus line in core. Free particles of coke and coal char were observed to drop from the void formed inside reacted pellets at 1 300°C or more. Free graphite particles were never observed from reacted pellets in any conditions. Recommended conditions for melting the reduced iron at low temperature were proposed.

(cf. *ISIJ Int.*, **44** (2004), 2001)

Reactions, coalescence of reduced Iron particles, and liberation of carbon particles in carbon composite iron ore pellets

Y.IGUCHI et al.

Reactions in carbonaceous material composite iron ore pellets of 18 mm heated at elevated temperatures were studied. The overall reduction rate is controlled by a complex combination of direct reactions and indirect reactions and never by gasification reaction. The final reduction of iron oxide is controlled by carburized carbon. The carburization of the reduced iron is mainly progressed by the direct carburization reaction, C(s)=[C]. As the carbon content approaches to the solidus line of the phase diagram of Fe–C system, the reduced iron particles are gradually forced to coalesce to grow in much larger particles. The coalescing rate is increased with temperature. Its driving force is the large surface energy of reduced iron due to its large specific surface area. Due to the coalescence, the particles of carbon are apt to lose the contact state with the reduced iron particles and to lose the ability to carburize the reduced iron. Therefore, the carburization exceeding the solidus line can be severely depressed. Consequently, the carburization up to the solidus line can be achieved at relatively lower temperatures, *i.e.* 1 200–1 250°C. As a result, the carbon content of reduced iron decreases with increasing temperature. Since the coal char has a very poor ability to directly carburize reduced iron, the carbon contents of reduced iron were very low and increased with increasing temperature. Graphite and coke possess the strongest and the intermediate carburizing abilities, respectively. And the carbon contents of the shell part and core part of reduced iron decreases with increasing temperature.

(cf. *ISIJ Int.*, **44** (2004), 2009)

Kinetics of the reactions in carbon composite iron ore pellets under various pressures from vacuum to 0.1 MPa

Y.IGUCHI et al.

In order to clarify the mechanism of the complicated reactions in carbon composite iron ore pellets, carbon composite iron ore pellets of 3.5 mm in diameter were heated in the five conditions; (a) in vacuum, (b) the closed system after evacuation, (c)–(e) the closed system of initially 0.001, 0.01 and 0.1 MPa nitrogen after evacuation. The weight loss was measured in the five conditions (a)–(e) by gravimetric method. The individual curves were composed of the fast first step and the relatively slow second step. The first step was analyzed as zero order reaction and the rate constant, k_{s1}, was obtained. The second step was analyzed by applying the rate equations for the diffusion control in the product shell of the shrinking core model for spherical iron ore particles. The applicability of the equations was pretty good. The rate constant, k_{s2}, was a function of the total pressure p_t and temperature T, which was expressed as $k_{s2}=A(p_t)\exp[-B(p_t)/T]$. The apparent activation energy was ranged from 195 to 280 kJ/mol, which is near the activation energy for the diffusivity of carbon in γ–iron. The rate of the fractional weight loss seems to be in a mixed

control regime of the direct reduction, indirect reduction and indirect gasification. The transition fractional weight loss from the first step to the second step was evaluated in the conditions (a) and (b). It decreased with increasing the total pressure until it reached nearly zero in the conditions (c), (d) and (e), where Eq. (11) was applicable in the whole range of F_t.

(cf. *ISIJ Int.*, **44** (2004), 2018)

Micro pore structure and reaction rate of coke, wood charcoal and graphite with CO_2

M.KAWAKAMI et al.

The reaction rate of coke, wood charcoal and graphite with pure CO_2 were obtained at 1 173 and 1 373 K. The change in the reaction rate, specific surface area and micro pore size distribution with reaction degree were examined. The results are summarized as follows.

(1) The specific surface area changes remarkably with reaction degree, while the reaction rate does not change so much.

(2) The change in the specific surface area accords well to the change in the volume of smaller pores than 10^{-8} m in diameter.

(3) The reaction occurs exclusively on the surface of pores between 10^{-8} to 10^{-6} m in diameter.

(4) The effective surface area for the reaction is from 0.064 to 0.25 of the total surface area.

(cf. *ISIJ Int.*, **44** (2004), 2028)

The effect of grain boundaries on iron nucleation during wüstite reduction process

M.BAHGAT et al.

Dense polycrystalline wüstite samples equilibrated with 50%CO–CO_2 gas mixture for 432 ks were reduced at 1 073 K using 75%CO–CO_2 to study iron nucleation process. Especially the effects of grain boundaries and grain orientations on the iron nucleation were focused. The orientation of surface grains in the wüstite specimens was measured by applying electron backscattering pattern technique. The number of formed iron nuclei near grain boundaries was found to be significantly larger than that away from grain boundaries. The prevalence of the iron nucleation process near grain boundaries was mainly due to the fast transport process of holes and Fe divalent cation by surface and grain boundary diffusion. The dominant effect of the grain boundary on the iron nucleation was found on the all grains with different grain orientations.

(cf. *ISIJ Int.*, **44** (2004), 2033)

TEM observation of the reduction of wustite by hydrogen ion implantation

N.ISHIKAWA et al.

The reduction process during hydrogen ion implantation into FeO (wustite) has been investigated by using a dual ion beam accelerator interfaced with a high voltage electron microscope (HVEM). Radiation damage and precipitates, which were generated during the hydrogen ion implantation were observed. The precipitates were generated by the reduction of wustite. The small precipitates had an orientation relationship with the wustite matrix while large precipitates became free from restrictions of the matrix.

(cf. *ISIJ Int.*, **44** (2004), 2039)

Kinetic analysis of iron carburizaiton during smelting reduciton

K.OHNO et al.

The most serious issues in the world are a large amount of energy consumption and generation of greenhouse effect gas from iron-making industry. The main factors of energy consumption are reduction of iron ore and carburization of reduced iron at high temperature. If it is possible to accelerate the rates of iron ore smelting reduction and the succeeding carburization at low temperature, the technology will be very valuable to lower energy consumption in the blast furnace.

It is well known that phenomena during smelting reduction are very complicated and the mechanism has not yet been clarified. Therefore, "*in-situ*" observation of smelting reduction and carburization of iron sample were carried out in our previous work. It was confirmed from the results that iron was carburized without a direct contact with carbonaceous material during smelting reduction. The mechanisms of this unique carburization were discussed and it was obtained a conclusion that formation rate of Fe–C particles caused by smelting reduction mainly determined the overall rate of iron carburization reaction.

(cf. *ISIJ Int.*, **44** (2004), 2043)

Effect of oxygen partial pressure on liquidus for the CaO–SiO_2–FeO_x system at 1 573 K

H.KIMURA et al.

Phase diagrams for the CaO–SiO_2–FeO_x system at various oxygen partial pressures are necessary for the design of raw material for ironmaking, the analysis of smelting reaction and ore sintering process. In this study, liquidus lines for the CaO–SiO_2–FeO_x systems at various oxygen partial pressures were observed at 1 573 K by using chemical equilibration technique. The liquid phase area changed with changing oxygen partial pressure from 10^{-3} to 10^{2} Pa (10^{-8} to 10^{-3} atm). The effect of Fe^{3+}/Fe^{2+} ratio on the melting mechanism is discussed.

(cf. *ISIJ Int.*, **44** (2004), 2050)

Formation rate of calcium ferrite melt focusing on SiO_2 and Al_2O_3 component

T.MAEDA et al.

The effect of the particle size of hematite on the formation rate of calcium ferrite melt and the dissolution rate of solid hematite into molten calcium ferrite were investigated. Without regard to the particle size of hematite, the addition of SiO_2 was more effective than the addition of Al_2O_3 for increasing the melting rate and reducing the melt formation temperature in calcium ferrite system. On the other hand, the addition of Al_2O_3 was more effective than the addition of SiO_2 for increasing the dissolution rate of solid hematite into the generated molten ternary calcium ferrite. The amount of dissolved hematite into molten calcium ferrite increased linearly with increasing the immersion time. The dissolution rate of solid hematite into molten calcium ferrite was mostly determined by Δ(mol%Fe_2O_3) that was considered to be the driving force of the dissolution and the effect of the revolution speed on the amount of dissolved hematite can be negligible. Therefore, the dissolution reaction of solid hematite at the reaction interface was the rate-controlling step under the condition of this study.

(cf. *ISIJ Int.*, **44** (2004), 2056)

Wetting and penetration behavior of calcium ferrite melts to sintered hematite

K.NAKASHIMA et al.

Effects of adding SiO_2 or Al_2O_3 on the wetting and penetration characteristics of calcium ferrite melts, $CaO \cdot Fe_2O_3$ (CF) and $CaO \cdot 2Fe_2O_3$(CF_2), to sintered hematite substrate have been examined. And the wetting and penetration characteristics were discussed from the viewpoints of the relation to the viscosity and surface tension of calcium ferrite melts. The effects of the addition of calcium ferrite slag with SiO_2 or Al_2O_3 on the strength of sintered hematite pellets were also examined.

The slag tablets of CF_2-based slag neither melt completely nor spread uniformly on the hematite substrate at the experimental temperature at 1 300°C in this study. The wettability of CF-based slag melts on sintered hematite substrate was improved by the addition of SiO_2 or Al_2O_3, and the spreading rate was increased with increasing the value of η/γ (viscosity/surface tension of slag melts). The penetration of CF-based slag melts into sintered hematite substrate was depressed by the addition of SiO_2 or Al_2O_3, and the penetration depth was increased with increasing the value of η/γ surface tension/ viscosity of slag melts). The sintered hematite pellet with CF–5 mass%Al_2O_3 slag sintered at 1 200°C had the highest compressive strength in this study. Because the liquidus temperature of CF slag is decreased to about 1 200 °C by adding 5 mass% Al_2O_3, and the sufficient amount of liquid phase, which has the appropriate wetting and penetrating characteristics controlled by the surface tension and the viscosity, as a binder was formed.

(cf. *ISIJ Int.*, **44** (2004), 2062)

Optimization of chemical composition and microstructure of iron ore sinter for low-temperature drip of molten iron with high permeability

K.HIGUCHI et al.

To discuss sinter condition for lowering dripping temperature of molten iron and enhancing reducibility, reduction behavior of sinter samples with extensive range of chemical composition was measured with reduction test under load. Basicity was found to have dominant influence on dripping temperature and should be in the range between 1.0 and 1.5. A further decrease in dripping temperature was achieved by decreasing Al_2O_3 content and increasing MgO content in sinter, which was related with low liquidus temperature, low viscosity and fast smelting-reduction of slag containing low FeO con-

tent. In contrast, reducibility and mineralogy of sinter influenced softening–melting behavior as well. Increasing fine pores could improve softening–melting behavior as a result of enhancing reducibility. Finally optimized sinter, containing 1.0–1.5 basicity, low Al_2O_3 and high MgO content was proposed. This chemical composition of sinter could lower dripping temperature by 80°C with fairly high permeability of sinter layer compared to conventional sinter. Possibility of the further improvement of softening-melting behavior at a constant chemical composition with controlling sinter mineralogy was discussed.

(cf. *ISIJ Int.*, **44** (2004), 2067)

Viscosity measurement of slag formed in the carbon-bearing iron oxide during the rapid heating

S.INABA et al.

Carbon-bearing iron oxide pellets with the acid component of slag are rapidly heated and reduced in the temperature of 1 623 K. The change of slag composition during the reduction is measured by the quantitative point analysis of EPMA. Viscosity of synthesized slag with as same as composition formed in the pellet are measured. The oscillating-plate viscometer is useful to measure the viscosity of slag with high FeO content.

(cf. *ISIJ Int.*, **44** (2004), 2077)

Lowering of thermal reserve zone temperature in blast furnace by adjoining carbonaceous material and iron ore

A.KASAI et al.

The improvement in the efficiency and the decrease in the temperature of reactions in the blast furnace have been required. Among the reactions, the solution loss reaction ($C+CO_2=2CO$) is an intensive endothermic reaction and controls the overall reaction inside the blast furnace. To realize the increase in the rate and the decrease in the temperature of the solution loss reaction, a technology to improve the reactivity of carbonaceous material by mixing it into packed ore bed, *i.e.* a technology to improve the reactivity by adjoining carbonaceous material and iron ore was fundamentally investigated.

Various kinds of carbonaceous materials were mixed into the packed ore bed and the starting temperature for the endothermic reaction equivalent to the solution loss reaction was measured on the basis of the principle of differential thermal analysis. Small size coke and carbon composite iron ore agglomerate as carbonaceous materials were mixed into the ore bed and the effect of carbon content in the ore bed and the effect of the degree of contact between carbonaceous material and iron ore were investigated. The following results were obtained.

(1) With the increase in the amount of carbonaceous material mixed into the ore bed, namely, in the carbon content in the ore bed, the starting temperature of the reaction is lowered.

(2) When the carbon content in the ore bed is constant, with the increase in the degree of contact between carbonaceous material and iron ore, the starting temperature of the reaction is lowered.

(3) Accordingly, it is expected that even when the carbon content in the ore bed is low, by mixing carbonaceous material into the ore bed to increase the degree of contact between carbonaceous material and iron ore, the temperature in the thermal reserve zone is lowered considerably. This results in the improvement of CO gas utilization efficiency and, as a result, the decrease in the reducing agents rate. The use of carbon composite iron ore agglomerate is promising as a means to realize the above expectation.

(cf. *ISIJ Int.*, **44** (2004), 2083)

Non-spherical carbon composite agglomerates: Lab-scale manufacture and quality assessment

M.NAKANO et al.

For recycling steel work dust and improving blast furnace (BF) performance, a few types of non-spherical carbon–iron oxide agglomerates were manufactured in laboratory scale and their strength and reducibility were evaluated using a shatter and a tumbler tester, a simulator for lumpy zone in BF and a softening/melting tester. The flat or ragged shape was expected to enhance reducibility and to prevent the agglomerate from unwilling rolling down to the center of BF.

Agglomerate in the shape of column with concave triangle cross-section (Tetra) showed the highest yield during extruding and almost same strength compared with a commercial spherical cold-bond pellet. In reducibility Tetra excelled sinter but spherical carbon composite pellet, which denied shape effect. Reduction disintegration of Tetra initiated at 600°C and reached to the maximum of 60% at 860°C, the entrance of thermal reserve zone, meaning the issue of cement bonding on disintegration remained unsolved. In case of single use, Tetra did not melt down up to the upper limit temperature of the softening/melting tester, causing S-value enlarged.

Using Tetra mixed with sinter was recommended as a trial of admixing 50% Tetra to sinter accelerate reduction rate of sinter, improving BF efficiency by 45 kg/t decreases in RAR; moreover, the mixture remarkably reduced the pressure loss of cohesive zone.

(cf. *ISIJ Int.*, **44** (2004), 2089)

Real microstructure molding for stiffness and strength analyses of texture in ores

T.AIZAWA et al.

Theoretical model is proposed to make stiffness and strength analyses for various multi-phase, porous media including the sintered ores. On the basis of the multilevel modeling, a macro-model is used to estimate the crushing strength of sintered ore with various compositions of texture. A micro model for each texture is constructed to represent its characteristic microstructure and to make stiffness and strength analyses. Since the real microstructure is taken into account of the unit cell, the homogenized stiffness provides us the elastic properties of textures with or without micro-pores. The stress analysis both for texture and crushing test-specimen, provides us the theoretical estimate of fracture strength, respectively. Three typical textures in the sintered ore are employed for application of the present theoretical models. The procedure to deduce the theoretical model from the optical micrograph is described for the texture of acicular calcium ferrite. Using the unit cell models for each texture, which is objective to the cell size and geometry, the stiffness and fracture strength are estimated. Assuming that the sintered ore specimen is composed of two phases or composite of porous hematite and slag-hematite complex, the fracture strength is also estimated as the function of volume fraction for porous hematite.

(cf. *ISIJ Int.*, **44** (2004), 2096)

Activities of Fe_xO within four-phase assemblages of the system $CaO–SiO_2–MgO–Fe_xO$

A.ISO-BAYASHI et al.

Towards better understanding of the reduction of iron oxide within blast furnace, a series of studies have been conducted. In this study, phase relationships for 4-phase assemblages of the system $CaO–SiO_2–MgO–Fe_xO$ was investigated, in conjunction with the measurements of the activities of Fe_xO *via* electrochemical technique incorporating magnesia-stabilized zirconia.

(cf. *ISIJ Int.*, **44** (2004), 2103)

Reduction behavior of FeO compact including molten slag

M.NAKAMOTO et al.

FeO compact including molten slag was reduced with H_2 at 1 500 K, and the effect of the slag penetration in the reducibility was investigated. Two kinds of molten slag, which coexist with solid FeO, in $FeO–SiO_2–CaO$ systems were used and the influence of the physical properties of molten slag, especially viscosity, on the reducibility was investigated. The penetrations of the molten slag with a low viscosity to the grain boundaries produce the spaces, which are useful as the pass of the reduction gas, in the interspaces between the grains. Then, the reduction rate of the FeO compact containing molten slag with a low viscosity is higher than that of the FeO compact containing molten slag with a high viscosity.

(cf. *ISIJ Int.*, **44** (2004), 2110)

Influence of gangue composition on melting behavior of coal-reduced iron mixture

T.MATSUI et al.

Iron ore particles on the graphite powder were observed by laser microscope to study low temperature reduction and melting behavior. The iron ores were classified two types by the gangue behavior through the reduction process. One forms a gangue concentrated layer and the other does not. Melting start temperature of iron ores with the gangue concentrated layer was higher than that of without. In the case of the iron ores with gangue concentrated layer, the formed gangue layer prevents the reduced iron from contacting with graphite, and the melting start temperature was much higher than the eutectic temperature of the Fe–C binary system. The melting start

temperature was lowered for the ore particle coated with $CaCO_3$ as the coated layer enhances melting of the gangue concentrated layer.

These results were confirmed by measurement of the softening and melt-down properties of the carbon composite iron ore briquette at a high temperature under-load test.

The direct contact of reduced iron with carbon is most important for the low temperature melting of iron ore. The selection of iron ore without gangue concentrated layer, flux addition to the iron ore with gangue concentrated layer will contribute to lowering the melt down temperature.

(cf. *ISIJ Int.*, **44** (2004), 2115)

Evaluation of viscosity of molten SiO_2–CaO–MgO–Al_2O_3 slags in blast furnace operation

M.NAKAMOTO et al.

The viscosity of molten SiO_2–CaO–MgO–Al_2O_3 slag was measured using a rotating cylinder method at high CaO and Al_2O_3 concentration regions to search for a slag with low melting temperature and low viscosity. The experimental results showed that the viscosity of molten 35mass%Al_2O_3–43.1mass%CaO–7.5mass%MgO–14.4mass%SiO_2 slag at 1 673 K was lower than 0.6 Pa·s that satisfies the fluidity in blast furnace operation.

The experimental results were compared with the calculated results of the viscosity model derived by the authors. The viscosity of molten SiO_2–CaO–MgO–Al_2O_3 system can be evaluated from our model in wide Al_2O_3 concentration range.

(cf. *ISIJ Int.*, **44** (2004), 2125)

Measurement of physical properties of slag formed around the raceway in the working blast furnace

S.INABA et al.

Slags around raceway were synthesized using reagents. The chemical compositions of the synthesized slags were chosen to be those of slags obtained from the working blast furnace. Viscosity, density, surface tension, wettability to coke and thermal conductivity of the slags were measured in order to investigate physical properties of tapping slags.

(cf. *ISIJ Int.*, **44** (2004), 2130)

Cold-model experiments on deadman renewal rate due to sink-float motion of hearth coke bed

H.NOGAMI et al.

With increase in pulverized coal injection rate to blast furnace, renewal behavior of deadman has been attracting much interests. This paper focuses on the renewal rate of the deadman induced by the sink–float motion of hearth coke bed, and it is discussed through cold-model experiments using half-cut model of blast furnace. Trajectories of packed particles in the deadman zone are converted into the transient velocity field, and further to the distribution of time required for particle transferring to the raceway zone. With this distribution the renewal rate of the deadman is quantitatively discussed. As the results, it is revealed that increase in the amount of accumulated water in the hearth, shallower hearth depth, and increase in gas flow rate make the discharging time of particles in the deadman zone shorter, and this tendency is explained by the height of sink–float motion of the hearth packed bed. About ten percent of particles that are discharged from the raceway passes through the deadman zone in the standard condition of this study. The particle movement induced by the sink–float motion of hearth packed bed is indispensable mechanism in the evaluation of deadman renewal.

(cf. *ISIJ Int.*, **44** (2004), 2137)

Activation of deadman state in the blast furnace using serpentine injection through tuyere

M.ICHIDA et al.

In the injection test of serpentine through one tuyere executed as a means to improve the furnace lower filling structure, the tuyere sampler insertion depth and the deadman temperature rose greatly by the amount of the fine serpentine injection of 20 kg/t or more. It is presumed for the melting point of slag piling up in the deadman surface part to decrease by the injection of fine serpentine through tuyere, for the fine ratio (−3 mm) of the melt origin and a slag hold-up ratio to decrease greatly, and for the gas and liquid permeabilities in deadman to have been improved. In addition, the possibility that the desulfurization reaction is able to be promoted efficiently while maintaining the active state of deadman and the possibility of the low temperature operation by the serpentine injection through tuyere were suggested.

(cf. *ISIJ Int.*, **44** (2004), 2144)

Effect of solution loss reaction on coke degradation rate under sheer stress

H.NOGAMI et al.

The degradation behavior of spherical coke samples was measured under sheer stress. The samples underwent the solution loss reaction until various degrees in several reaction temperatures (10–30 wt% and 1 273–1 573 K). A sample is settled between two horizontal boards with parallel grooves like washboard. The sheer stress was applied to the sample by sliding upper board at a certain cycle with a constant vertical load. The generated powder was sieved and weighed, and the appearance of the coke sample was observed. From the measurement of the powder generation rate and discussion on the reaction mode of the solution loss reaction, the degradation behavior can be explained by the distribution of local reaction degree within a coke particle. The powder generation rate from the samples reacted in lower temperature increases with increase in overall reaction degree because the reaction of coke substrate with carbon dioxide, namely the strength deterioration, proceeds in entire particle. The high temperature samples show little increase in the powder generation with the overall reaction degree since the surface reaction mode increases local reaction degree in the vicinity of particle surface and this reacted layer is also consumed from the surface. This dependency of the powder generation behavior on the reaction mode of the solution loss reaction measured in this study corresponds to the previously reported behavior in the raceway zone regardless of grinding mechanism. Therefore, it is considered that the single-particle degradation test of coke is an appropriate method to measure the degradation behavior of a coke particle under sheer stress.

(cf. *ISIJ Int.*, **44** (2004), 2154)

Raceway design for the innovative blast furnace

H.NOGAMI et al.

This study tries to design the combustion zone in the highly efficient blast furnace for aiming at great reduction of energy consumption and environmental loads by use of raceway mathematical model. The model treats strictly the discontinuous movement of lump coke particles inside and around raceway, and it considers heat exchange with gas and chemical reactions with gas.

In this study, first, the verification of the model is performed. Next, the controllability of raceway by blast conditions is investigated. Finally, the raceway in the top gas recycling process is evaluated in terms of the suitability as combustion zone of the novel blast furnace and of the possibility of its realization. The gas recycling process has the characteristic of blowing top gas without CO_2, pure oxygen and plastics from tuyere. The results obtained in this work are as follows.

1) Raceway mathematical model has the sufficient ability to represent the characteristics of raceway in all cokes operation and PCI operation.

2) The shape and size of raceway and gas temperature in raceway can be controlled by blast temperature and gas compositions. In addition, nitrogen enrichment in blast is effective to form the uniform and low temperature combustion zone.

Raceway in top gas recycling process becomes larger, gas temperature in and around raceway is lower and volumetric flow rate of bosh gas is less than conventional process. Therefore, raceway conditions in the recycling process enable high productivity and high efficiency.

(cf. *ISIJ Int.*, **44** (2004), 2160)

Numerical analysis on blast furnace performance under operation with top gas recycling and carbon composite agglomerates charging

M.CHU et al.

The blast furnace operations with top gas recycling, carbon composite agglomerates (CCB) charging, cold oxygen blast and waste plastics injection are numerically evaluated by means of multi-fluid blast furnace model on the premise of constant raceway conditions and hot metal temperature. These evaluations are in comparison with conventional operation. Simulation results reveal that CCB charging and/or cold oxygen blast lead to low temperature level in the shaft region, which retards the reduction of CCB. On the other hand, injection of waste plastics enriches hydrogen gas in the furnace. And top gas (after CO_2 removal) recycling tremendously enhances the concentrations of H_2 and CO in the whole furnace, which greatly promote the indirect reduction of sinter in shaft despite lower tempera-

ture. Under the innovative operations, the efficiency of blast furnace shows evident improvement, especially in the case with simultaneous injections of treated top gas through shaft and tuyere. The model computations predicted that total heat input decreases while the productivity increases under the operation with top gas recycling. Additionally, top gas recycling and waste plastics injection also contribute to considerably reduce carbon dioxide emission. It is expectable to develop high efficiency blast furnace with improved productivity and lowered environment load through exploiting the processes presented in this study. If scrubbing and fixing of CO_2 and manufacturing of process oxygen are commercially available, these innovative processes will possess broad applying potential.

(cf. *ISIJ Int.*, **44** (2004), 2169)

Design of innovative blast furnace for minimizing CO_2 emission based on optimization of solid fuel injection and top gas recycling

R.MURAI et al.

The concept of innovative ironmaking process for aiming at energy half consumption has been proposed based on the basic experiments and mathematical calculations. For innovative ironmaking process, intensive combustion technology around raceway was examined by hot model experiments and three-dimensional mathematical simulation so as to utilize solid fuel such as plastics effectively. As results, it became clear that simultaneous injection of pulverized coal / plastics or pulverized coal / gas fuels is favorable to improve combustion efficiency remarkably. Decrease in thermal reserve zone temperature and top gas recycling besides plastics injection are found to be effective for lowering coke rate. In this process, productivity can be also improved owing to relaxation of flooding condition in the lower part of blast furnace. Productivity of 3.5 and more, that is determined by fluidization condition at top, can be expected in this sinnovative ironmaking process. Totally, it is evaluated that amount of carbon emission would be reduced by eighty-six percent provided sequestration of carbon dioxide is implemented. Finally, integrated ironmaking process with co-generating oxygen production process was proposed.

(cf. *ISIJ Int.*, **44** (2004), 2178)