

Fundamentals of High Temperature Processes

Effect of aluminum and oxygen content on diffusivity of aluminum in molten iron

M. KAWAKAMI *et al.*

The diffusivity of aluminum in molten iron has been obtained with the capillary reservoir method. It is given as

$$D \text{ (m}^2\text{/s)} = (1.00 \pm 0.11) \times 10^{-6} \exp(-81\,500/RT) \\ 1\,823 \text{ to } 1\,923 \text{ K}$$

at lower oxygen content than 0.025 mass% and lower aluminum content than 1.4 mass%. If the oxygen content is higher, the diffusivity decreases apparently with the oxygen content. The effect of oxygen on aluminum diffusion is well interpreted by the counter current diffusion model. The effect of aluminum content is well expressed by the Darken's equation.

$$D = (N_{Al}D_{Fe}^s + N_{Fe}D_{Al}^s) \left(1 + \frac{d \ln \gamma_{Al}}{d \ln N_{Al}}\right)$$

The self diffusivities of Fe and Al in the equation are obtained, respectively as

$$D_{Fe}^s \text{ (m}^2\text{/s)} = 9.48 \times 10^{-4} \exp(-145\,000/RT)$$

$$D_{Al}^s \text{ (m}^2\text{/s)} = 1.54 \times 10^{-6} \exp(-96\,000/RT)$$

Ironmaking and Reduction

Integrated mathematical model of pulverised coal combustion in a blast furnace

K. TAKEDA *et al.*

The shortage of coke production due to the closure of coke ovens has led in Japan and other industrialised countries to increasing the injection of auxiliary fuels, *e.g.* pulverised coal (PC) into blast furnace tuyeres. The PC injection at high rates of more than 200 kg/t requires high burnout within the raceway zone. In order to analyse flow and combustion in the raceway and to assist improvement of burner design, a two-dimensional mathematical model of PC combustion has been developed with simulating both the blowpipe and raceway.

Effects of a packed bed on the turbulent features of gas and particulate flow were introduced to the model along with all other pertinent phenomena such as heterogeneous reactions of coke and char particles. Validation work against measurements in two industrial blast furnaces indicated that the model has worked satisfactorily for simulation with and without PC injection.

Various measures for burnout improvements were explored under an injection rate of 200 kg/tHM. Notable improvements were observed by oxygen enrichment to the secondary air and enlargement of the outer diameter of the injection burner.

Three dimensional modelling of the wall heat transfer in the lower stack region of a blast furnace

G.X. WANG *et al.*

This paper describes a mathematical model, together with its solution technique developed by the finite element method, to simulate the three-dimensional heat transfer in the wall of the lower stack region of a blast furnace, with the wall consisting of criss-crossing refractories and water-cooling components. The approach is validated by the good agreement between the computed and measured radial temperature distributions, and subsequently used to study the heat transfer process under various water-cooling and blast furnace operating conditions. The results indicate that the heat transfer and hence the wear process in the furnace wall can be controlled by properly adjusting blast furnace operating conditions, such as the cooling water supply and the gas flowrate of blast furnace.

Structure of sinters from complex Chinese iron ores

L.X. YANG *et al.*

Domestic iron ores and sinters from six mills in PRC have been evaluated. A large number of the ores consist of dense magnetite and hematite, and complex iron ores containing minerals including pyrite, pyrrhotite, biotite and siderite. One particular ore was extremely complex containing a high level of fluorite. Based on the sinter samples received, one sinter was obviously produced from predominantly magnetite blends as silicate glass and SFCA of high temperature morphology were the major bonding phases present and the major iron oxide mineral was magnetite. For the plants using predominantly hematite ore in their blends, SFCA is relatively well developed and the sinters also have a very high level of relict hematite. Sinters with this are characterised by high reducibility and a good strength. However, such a sinter structure is not formed automatically when a high level of hematite is present in the blend. The structure of three sinters indicated that when coke rate is high such a structure is not achievable although high temperature morphology SFCA is developed. The sinter produced from ore containing high fluorite is the most reducible but is also extremely weak. The strength of the different mineral phases in the sinters were characterised using indentation techniques. Good correlations were obtained between tumble indices of the sinters and a composite fracture toughness of the major phases. The study also showed that some of the more typical structures found in these plant sinters could be reproduced using a bench-scale furnace under controlled conditions.

A mathematical model of four phase motion and heat transfer in the blast furnace

P.R. AUSTIN *et al.*

A two dimensional mathematical model is developed describing four phase motion and heat transfer in the blast furnace. The four phases are gas, lump solid, liquid and powder. The model includes simple representations of the major chemical reactions and physical structures within the furnace. It calculates the steady state velocity, temperature and volume fractions of all four phases. The model is able to allow for the influence of the behaviour of each phase on that of every other phase. In particular, it can predict how the behaviour of one phase may change in response to a modification to another phase's behaviour.

Steelmaking and Refining

The hydration kinetics of lime

A. MACIEL-CAMACHO *et al.*

Hydration rate of calcium oxide has been investigated for a suspended single pellet into an atmosphere of air with a controlled humidity using a computer aided thermo-gravimetric technique. It has been found that the hydration reaction takes place on a sharp, well defined interface between the product layer and the unreacted core. A theoretical model for this reaction, that takes into account the sample swelling, was derived and employed to estimate the values for the rate constant and the effective diffusivity of the water vapor in the Ca(OH)₂ layer.

These results suggest that gas mass transfer, pore diffusion and chemical reaction were all contributing resistances in the model. The calcination temperature and the water vapor partial pressure are the two most important variables that affect the hydration rate of lime.

The higher the calcination temperature, the lower the hydration rate and the higher the water vapor partial pressure, the higher the hydration rate. The hydration temperature was found to play also a very important role in the phenomena involved.

The hydration kinetics of recarbonised lime

A. MACIEL-CAMACHO *et al.*

The hydration rate of partially recarbonized lime pellets has been studied by employing a single pellet into a stream of air/vapor water mixtures using a computer aided thermo-gravimetric technique. The hydration reaction takes place on a sharp, well defined interface between the product layer and the unreacted core.

It has been found that the hydration mechanism consists in two steps. The first observes very slow hydration rates and the second higher ones. During the first step the water molecules diffuse through a close porous carbonate structure and the second one begins

when these molecules reach the calcium oxide-calcium carbonate interface to continue through the lime core. A theoretical model was derived to explain the results of this study. The experimental results were acceptably well predicted with calculations performed using this model.

On the other hand, it was found also that the higher is the lime calcination temperature the thinner is the recarbonized layer formed even under high CO₂ partial pressures. However, these thin layers are more effective to increase the hydration resistance of lime pellets than thicker ones. This is an important experimental finding since it indicates that low recarbonization extents are good enough to increase the hydration resistance of steelmaking lime without impairing its quality.

Viscosities of LF slags and their impact on ladle refining

P.G. JÖNSSON *et al.*

This study focuses on the viscosities of synthetic slags used in secondary refining operations. Typically, these slags contain mainly CaO, Al₂O₃, MgO and SiO₂. The data for LF slag viscosities are used in a model for a gas-stirred ladle to evaluate the effect of viscosity variations on predicted parameters close to the slag/steel interface. The results show that viscosities of LF slags significantly affect ladle refining operations. It is therefore necessary to control the composition of the synthetic slags carefully during production.

Analysis and Characterization

Predictable modelling of heat transfer coefficient between spraying water and a hot surface above the Leidenfrost temperature

H. FUJIMOTO *et al.*

In order to evaluate the cooling intensity of water spray impacting on a hot metallic surface above the Leidenfrost temperature, the formulation of heat transfer coefficient in the forced convection boiling region has been made as a function of the droplet size, the impinging velocity and the number density of droplets whose parameters are independent of each other. So far, many works on the mist/spray cooling process have been made, in particular, from an experimental point of view. However, the general procedure capable of evaluating heat transfer rate between a hot metallic surface and water spray has not been established yet, because there are a large number of parameters affecting the spray cooling process.

Then, we have experimentally derived a new formula consisting of the above three parameters to be dominant for heat transfer rate in the spray cooling process. The stainless steel surface heated to about 900°C has been cooled by water spray of ~20°C and the time history of the surface temperature has been measured.

We have selected some kinds of full cone nozzles whose characteristics such as the average droplet diameter, the velocity and the distribution of water flux have been different from each other, and performed the cooling tests using them. Finally, the formula capable of giving best-fit to the experimental results has been proposed. The effect of the spraying characteristics on the heat transfer rate has been discussed from an experimental point of view.

Forming Processing and Construction

Effects of extreme pressure additives on lubricity and anti-seizure property of lubricants

S. HAN *et al.*

The effects on lubricity and anti-seizure property of lubricants according to base oils and EP additives of sulfur and phosphorous types in cold rolling were evaluated by a laboratory scale rolling mill, where the contact conditions between work roll and strip are very close to an actual cold rolling mill. The following experimental results were obtained. Sulfur type EP additive improves lubricity better than phosphorous type. In contrast, phosphorous type EP additive improves anti-seizure property better than sulfur type. And anti-seizure property is not affected by the kinds of base oil, but improved by the kinds and the amount of EP additives. Therefore, the amount of EP additives of sulfur and phosphorous types must be controlled in order to improve both lubricity and anti-seizure property. In addition, the existence of EP film was verified from the results of EDS analysis of the Falex test pins.

Surface Science and Technology

Relation of texture formation of TiN films and crystallographical character in several steel matrices

Y. INOKUTI

In order to clarify the difference in the texture formation of the TiN films deposited on various steel matrices, TiN ceramic coating was done on the surface of a polished (011) [100] single crystal of silicon steel, grain oriented silicon steel, SUS 304 and SUS 430 stainless steel sheets and interstitial free (IF) steel sheets. Pole figures of dual textures of the TiN films and related steel matrix samples were measured simultaneously using a solid state detector (SSD) auto pole figure apparatus.

{111}_{TiN} pole figures of the TiN films deposited onto the surface of a (011) [100] single crystal of silicon steel and grain oriented silicon steel sheet showed the dominant texture of (111) [110] orientation, whereas the {100}_{SI-steel} pole figure of the silicon steel matrices showed the dominant texture of (011) [100]. Subsequently, {111}_{TiN} pole figure of the TiN films deposited on the surface of the

SUS 304 stainless steel sheet showed a weak texture of (111) [110], and {100}_{Stainless steel} pole figure of the SUS 304 stainless steel sheet showed the texture of (112) [111]. Moreover, the {111}_{TiN} pole figure of the TiN films deposited on the surface of SUS 430 stainless steel showed the texture with a very weak {111}_{TiN} plane and that of IF steel sheets showed no preferred orientation.

From these results, it is concluded that texture formation of TiN films takes place preferentially when these films have a good coherency with steel matrices.

Zn/Ni electrodeposition on low carbon steel substrate

H. OHTSUBO *et al.*

Zn/Ni alloy electrodeposition on a low carbon steel sheets has been examined by means of X-ray diffraction and scanning electron microscopy.

With increasing current density, Ni content in a Zn/Ni film deposited decreases to a minimum value and then increases. This variation of Ni content in lower Ni baths corresponds to the morphological change of the deposits from granular η/γ mixed phases to layered hexagonal η -phase plates. But in the case of higher Ni baths, the deposited films comprise both η - and γ -phases, and the morphology varies from fine granular precipitates to large spherical particles consisting of granular precipitates. The c/a ratio of η -phase crystal varies from 1.87 to 1.75 with increasing the supersaturation of Ni atoms in η -phase deposits. The effects of quantity of electricity on Ni content of the deposits can be explained in terms of the variation of surface area of the deposits.

Physical and Mechanical Properties

Transformation behavior and damping capacity in Fe-17% Mn-X% C-Y% Ti alloy

S.-H. BAIK *et al.*

Effect of carbon and Ti on $\gamma \leftrightarrow \epsilon$ martensitic transformation behavior and damping capacity is investigated in an Fe-17Mn alloy.

The suppressive force of carbon against $\gamma \rightarrow \epsilon$ transformation increase linearly with an increase in its content, lowering Ms temperature and volume fraction of ϵ martensite. Carbon deteriorates damping capacity by reducing the area of γ/ϵ boundaries and mobility of the boundaries contributing to anelastic deformation. The reduction in the mobility of the boundaries is accelerated when carbon-containing alloy is aged at higher temperatures than room temperature.

The effect of Ti on damping capacity is found to be beneficial in carbon-containing alloy, which is attributed to the depletion of carbon solute due to the formation of TiC.

Effect of copper and tin on hot ductility of ultra-low and 0.2% carbon steels

C. NAGASAKI *et al.*

The hot ductility of ultra-low carbon steels and 0.2 % plain carbon steels containing copper and/or tin has been investigated at elevated temperatures ranging from ferrite region to lower austenite region and at various strain rates. Ultra-low carbon steels generally exhibit good ductility regardless of copper and tin additions except for the lower austenite temperature range, where the addition of tin decreases the ductility slightly. The plain carbon steel containing 1.0 % copper also exhibits good ductility, except for a ductility trough around 1 050 K and at 10^{-2} s⁻¹. Recrystallization results in the improvement of ductility above 1 180 K and at 10^{-2} s⁻¹. The plain carbon steel containing 0.2 % tin shows good ductility at 200 s⁻¹, but exhibits a ductility trough in the lower austenite temperature range below 1

s⁻¹. At the strain rate of 10^{-2} s⁻¹, the embrittlement takes place most severely at 1 080 K, which corresponds to the transition temperature from austenite to ferrite. The embrittlement with intergranular fracture occurs in the specimen with low reduction in area. Initial cracking is observed at grain boundaries without proeutectoid ferrite. The addition of tin can prevent grain boundary migration or dynamic recrystallization by its grain boundary segregation, which leads to decrease in ductility.

Social and Environmental Engineering

Direct conversion of blast furnace gas to dimethyl ether over Cu-ZnO-Ga₂O₃/γ-Al₂O₃ hybrid catalyst : Optimum mass ratio of the catalyst

S. MACHIDA *et al.*

The objective of this study is to develop a catalyst in a packed-bed reactor for direct

synthesis of dimethyl ether ((CH₃)₂O.DME) from blast furnace offgas (CO-CO₂-H₂-N₂, BFG). Physically-admixed (hybrid) catalysts of Cu-ZnO-Ga₂O₃ for CH₃OH synthesis and γ-Al₂O₃ for its dehydration were experimentally studied, in which the influence of mixing ratio of the two catalysts on both yield and selectivity of DME was mainly examined for the same catalyst mass. The results showed that the developed hybrid catalyst is very effective in producing DME directly from simulated BFG to avoid equilibrium limit of methanol. Interestingly, the yield of DME had a significant dependence of mixing ratio, and the hybrid catalyst with only 5 mass% γ-Al₂O₃ showed the highest yield with 99.3 % selectivity of DME+methanol. This implies that methanol formation governs the rate of this series reaction (BFG→CH₃OH→DME) due to fast dehydration of methanol to DME.