Fundamentals of High Temperature Processes

Manganese and phosphorus equilibria between liquid copper and MnO-P_2O_5 slag

A. SOBANDI et al.

The liquid copper alloys containing 0.2~1.0 mass% Mn and 0.03~0.5 mass% P were equilibrated with MnO saturated and unsaturated MnO-P_2O_5 slags in a molybdenum crucible under a flowing CO_2/CO or CO_2/H_2 atmosphere in the temperature range of 1 523 to 1 673 K.

Manganese-phosphorus and manganese-manganese interaction parameters in liquid copper were found at 1 623 K as follows:

$e_P^{Mn} = -0.010 \quad e_{Mn}^{P} = -0.021 \quad e_{Mn}^{Mn} = 0.027$

These values were examined by considering the relationships among oxygen partial pressure, the activities of manganese and phosphorus in liquid copper. The standard free energy changes for the reduction of solid MnO, MnO(s)=Mn+1/2 O_2(g), and the dissolution of pure liquid manganese in liquid copper, Mn(l)=Mn, were determined as a function of temperature.

The activities of MnO and P_2O_5 in MnO-P_2O_5 slags were measured at 1 573 K as a function of the composition. The temperature dependence equation of the P_2O_5 activity was also derived in the MnO saturated condition. On the basis of the present results, examination was done concerning phosphorus and manganese equilibria between hot metal and the MnO-P_2O_5 slag.

Ironmaking and Reduction

Microstructures of self-reducing pellets bearing iron ore and carbon

R.C. NASCIMENTO et al.

The steps Fe_2O_3➡Fe_3O_4, Fe_3O_4➡"FeO" and "FeO"➡Fe, during the reduction of self reducing pellets plus charcoal (with volatile matter), between 1 223-1 423 K, were analysed. It was found that typical microstructures of the step Fe_2O_3➡Fe_3O_4 consisted of transgranular cracks in the hematite particles and the Fe_3O_4 morphology was probably lamellar. The microstructures of the step Fe_3O_4➡"FeO" were similar to and dependent on the first step of reduction and it was observed the formation of superficial microcracks in the "FeO" phase. The typical morphology in the step "FeO"➡Fe was that of Fe whiskers between 1 223-1 323 K, but at 1 423 K the found morphology was a mixed one, that is a dense morphology (clusters of cone shaped whiskers) adjacent to a porous morphology of iron.

Sintering reactions of magnetite concentrates under various atmospheres

L. YANG et al.

Sintering reactions of magnetite concentrates were studied under various atmospheres using a bench-scale infrared heating furnace. The results show that the ability of magnetite to participate in reaction (reactivity) is dependent on gangue level and gangue minerals in the ore, and magnetite in easy-fusing ores has a high reactivity. The reactivity is remarkably improved by sintering in oxidising atmospheres without increasing temperature.

Calcium ferrites can form prior to the oxidation of magnetite in atmospheres with very low oxygen partial pressure ($p\ O_2$). In the present of silica, the amount of calcium ferrites formed by this mechanism can be negligible. The resulting sinters consist predominantly of magnetite and silicates. If cooled in high $p\ O_2$ after sintering in N_2, significant SFCA (silicoferrite calcium and aluminium) forms and becomes the major bonding phase. The SFCA formation mechanism is likely to be *via* reactions of magnetite and melt in the presence of oxygen. This is considered to be the main route of SFCA formation in magnetite sintering.

Most of the magnetite is oxidised to hematite in an oxidising atmosphere. Mineral formation in sintering of oxidised magnetite is similar to that observed for hematite in terms of dependencies on temperature, basicity and alumina content. Based on observations in this work, the following are suggested to develop SFCA and improve sinter quality in magnetite sintering: (1) increase the hematite level in ore blend; (2) develop magnetite oxidation; and (3) adopt low coke and oxidising atmosphere sintering practice.

A commercial production test of iron ore sinter using high amounts of pisolite ores and quality evaluation of the sinter products

N. SAKAMOTO et al.

To utilize pisolite ores as raw materials of iron ore sinter, a commercial production trial was carried out by designing the structure of quasi-particles. Main results obtained from the trial are summarized as follows:

(1)The commercial production test using 40 mass% pisolite ores in raw materials showed that high quality sinter was produced by making quasi-particles having duplex structures; the inner core is granulated by raw materials containing the pisolite ores and the outer shell is coated with both coke fine and high grade magnetite ore fines.

(2)According to the reduction kinetic analysis of sinter products, high reducibility of the products produced from quasi-particles having the duplex structure results in the improved reduction rate parameters resulting from the product structures containing many micro-pores ranged from 10 to 100 μm.

(3)Improved reduction degradation characteristics of the products depend on decreased hematite phase and increased magnetite phase in the sinter structures as well as micro-pore distributions.

Steelmaking and Refining

A mathematical model for the reduction kinetics of iron oxide in electric furnace slags by graphite injection

R.D. MORALES et al.

A three-phase, solid-gas-liquid, reactive jet is mathematically modeled in time domain for the injecting operation of graphite particles in complex electric furnace steelmaking slags to reduce the iron oxide contents. The model takes into account the jet penetration in the liquid, the physical changes that the slag suffers due to chemical composition variations, the surface active effects of silica in molten slags and the coupling-uncoupling flow characteristics between the carrier gas and the solid particles in the molten phase.

The mathematical simulations indicate that at small particle sizes (100-150 μm) the reaction kinetics is controlled by the gas-melt interface, under this regime acid slags show higher reduction rates than basic ones. At larger sizes this reaction is controlled by the mass transfer of iron oxide from the bulk phase to the gas-melt interface and basic slags show higher reduction rates than acid ones. To obtain a given reduction rate of iron oxide there is an optimum particle size at which the consumption rate of the reducing agent is minimum. Below this size the particle is consumed by the reaction without reaching high efficiencies. Above this minimum the particle size is so large that it exits the molten bath only partially reacted decreasing also the efficiency of the reaction. Just at this minimum the particle is totally consumed by the reaction with a minimum consumption rate of the reducing agent.

Prediction of emptying flows in ladles and verification with data from trace element plant trials

C.-E. GRIP et al.

A three-dimensional mathematical model of a casting ladle based on fundamental transport equations has been developed. The model may be used for predictions of both a standing ladle and a ladle from which steel is teemed into a tundish. An additional feature of the model is that it can predict concentration profiles of tracer elements which are added to the steel. The predicted concentration profiles during teeming are compared to experimental data from plant trials performed at SSAB and the agreement is found to be good. The model is used as a tool in the development of process control models.

Particle removal from liquid phase using fine gas bubbles

X. ZHENG et al.

Cold model study was undertaken to investigate the particle removal from the liquid phase using fine gas bubbles. Fine gas bubbles were created by flowing water through a tube in which a constriction was implanted, and injecting air underneath the constriction. The strong turbulent conditions underneath the constriction warranted formation and dispersion of fine bubbles in the tube. It was found that the probability of attachment of particles to bubbles in the tube was unity. When the aggregates of particle/bubble were discharged into the bottom tank where an abrupt change occurred in their relative movements, large particles were detached from the bubbles due to high inertial force and penetrated into the liquid in the tank, while small particles were kept attached to the bubbles and quickly floated up to the free surface of the tank. Under the present experimental conditions, polystyrene particles smaller than 500×10^{-6}m in diameter were mostly kept attached to the bubbles and floated up to the free surface of the bottom tank, while the ones larger than 500×10^{-6}m were detached from the bubbles and remained in the tank, circulating with water. This was in good agreement with the results predicted by the mathematical model reported previously. The wettability of a particle with the liquid was found to be an important factor in determining the removal efficiency of particles by attachment to bubbles. It was demonstrated that the process employed in the present study can be an effective technique for removing non-metallic inclusions from molten metals such as steel.

Casting and Solidification

Modeling of microstructural evolution in squeeze casting of an Al-4.5mass%Cu alloy

I.-S. CHO et al.

A stochastic model based on the coupling of the cellular automaton technique with the finite volume method was developed to simulate the formation of solidification grain structures in the squeeze casting of an A1-4.5mass% Cu alloy. The present model was also applied to predict the CET (columnar-to-equiaxed transition). The interfacial heat transfer coefficients between the casting and the die were evaluated as a function of time using an inverse problem method. Solidification sequences in squeeze casting were simulated using the calculated interfacial heat transfer coefficients. The effects of casting process variables on the CET and the solidification grain structures in squeeze casting of an A1-4.5mass%Cu alloy were investigated. The predicted solidification grain structures were in good agreement with those obtained experimentally. It was found that the CET can be predicted using the concept of the interface velocity at the solidification front.

A numerical model for cooling rate dependence of the degree of undercooling during rapid solidification of 18Cr-8Ni stainless steel

H. FUJINO et al.

Cooling rate dependence of the degree of undercooling at the onset of solidification for 18Cr-8Ni stainless steel was numerically analyzed using a classical nucleation theory. Transient time which can characterize the time-dependent behavior of nucleation was evaluated for iron. It is shown that temperature change in the experiment is slow enough against the transient time and no time-dependent behavior can be expected within the predictions by the classical theory. A new model for time-dependent contact angle was proposed so as to reproduce the cooling rate dependence of the degree of undercooling. This prediction model shows a good agreement with the experimental result for 18Cr-8Ni stainless steel. The effect of substrate temperature on the degree of undercooling and the primary nucleation phase of 18Cr-8Ni stainless steel was also discussed using the model.

Electromagnetic control of initial solidification in continuous casting of steel by low frequency alternating magnetic field

T. TOH et al.

A marked improvement of the surface quality of casts and a break-through in casting speed in conventional continuous casting of steel require the introduction of new technology for initial solidification control. The authors have approached these problems by the use of electromagnetic shaping of the meniscus and demonstrated the possibility using simulation experiments. This paper describes the results of numerical prediction of the effect of electromagnetic field on the initial solidification of steel and the experimental results obtained by continuous casting of round austenite stainless steel billets of 180 mm diameter with solenoidal magnetic field with main frequency, 60 Hz. The numerical results concerned with magnetohydromagnetics and heat transfer phenomena predicted improvement of the surface roughness of the cast billet and improvement of mold lubrication by decreasing the dynamic pressure due to the meniscus shaping effect. In the experimental casting, the surface of billets were smoothed and the mold friction force was reduced by imposing the magnetic field, which are in consistent with the numerical predictions.

Instrumentation and Control System

Principle and application of the pyrometry by use of function fitting method to thermal radiation spectra

S. KOBAYASHI et al.

It is not difficult to observe spectra of thermal radiation emitted from a hot surface. It is very interesting to develop the pyrometry to determine the temperature on the basis of thermal radiation spectra. There is not yet sufficient theoretical analysis for the pyrometry, which was termed the spectrum method in this paper. This method also will not be free from the so called emissivity problem. For solving this problem, this method assumed a linear wavenumber-dependence of the emissivity. The theoretical analysis predicted that there was the particular linearity that led to no temperature determination. The present work described the requirements for permissible linearity. The conventional two-color method assuming constant emissivity was applied to the spectrum data and the determination errors due to the deviation from the constant were estimated.

A temperature-emissivity diagram was made to show the applicability arrangement of the spectrum and the two-color methods in the spectrum pyrometry. It was found that these methods were able to play complementary roles to determine temperatures. This diagram was useful for predicting the feasibility of temperature measurement.

A temperature measurement technique combining both methods was proposed and applied to silicon carbide tube and platinum ribbon heaters. This technique proved to be useful, although it still needs more accumulation of empirical knowledge about how to choose wavenumber range.

Microstructure

Identification of Ti-S-C-containing multi-phase precipitates in ultra-low carbon steels by analytical electron microscopy

M. HUA et al.

The Ti-, S-, and C-containing particles in ultra-low carbon(ULC) interstitial free steels are frequently multi-phase in nature, consisting of TiS(9R) and $Ti_4C_2S_2$(H), and, therefore, show an irrational Ti/S ratio as detected by a X-ray energy dispersive spectrum(EDS). This paper confirmed the existence of multi-phase precipitates in ULC steels by analytical electron microscopy. It is shown that an accurate description of 9R-H two-phase composite particles can only be achieved when particles are at some special orientations.

Service-induced changes in the microstructure and mechanical properties of a Cr-Mo-Ni-V turbine steel

M. YAMASHITA et al.

The effect of service temperature on the degradation of mechanical properties of a low alloy Cr-Mo-Ni-V steel applied for turbine

rotor, retired after 15.8 years of service was evaluated and supplemented with the results from microstructural and fractographic examinations. Maximum embrittlement, manifested as decrease in upper shelf energy and increase in ductile-to-brittle transition temperature had occurred at a service temperature of 714 K and the material serviced at 811 K exhibited relatively better toughness. A re-aging treatment at 811 K for 24 h partially recovered the loss in toughness . The dominant carbides identified were $M_{23}C_6$ and M_6C, enriched with chromium and iron, and molybdenum and iron, respectively and M_2C with molybdenum and vanadium as the major metallic constituents. Coarsening of carbides occurred with increasing temperature through carbide reactions. The embrittled material showed the presence of coarse $M_{23}C_6$ carbides along the prior-austenite grain boundaries. However, material serviced at 811 K contained relatively less coarse grain boundary precipitates. Homogeneous precipitation of fine carbides of M_2C type also occurred at this temperature through carbide reactions. Re-aging of the embrittled material led to partial dissolution of grain boundary carbides and also to copious precipitation of M_2C type of carbide. Observed changes in mechanical properties are partly attributed to the in-service evolution of carbides and partly attributed to segregation of impurities at grain boundary.

An experimental and theoretical investigation of diffusion across a joint of two multicomponent steels

T.HELANDER et al.

Diffusion across a joint of a stainless steel and a low alloy steel has been studied experimentally at 1 100 and 1 250°C. Precipitates that formed as a result of the interdiffusion have been identified as $M_{23}C_6$. Concentration pro files have been measured and the microstructure has been studied. The experimental results are compared with computer simulations based on thermodynamic calculations of phase equilibrium (CALPHAD) and driving forces for diffusion combined with a numerical solution of the multicomponent diffusion equations. Despite the fact that no adjustable parameters have been introduced in the simulation the agreement between experimental results and simulations is satisfactory. It is thus concluded that the structural changes close to the joint may be essentially predicted from fundamental thermodynamic and diffusivity data even for the present combination of alloys involving 6 major components which were all included in the simulations.

Physical and Mechanical Properties

Effects of W addition and heat-treatment on corrosion fatigue crack growth behavior of duplex stainless steels

C.S.LEE et al.

The corrosion fatigue crack growth (CFCG) behavior of a duplex stainless steel with both homogenized and aged microstructures has been studied using the single edge notched specimens tested in 3.5 % NaCl solution. The emphasis is put on the effects of the substitution of W for Mo and the isothermal aging treatment on the CFCG properties. It is found that the apparent CFCG resistance is markedly improved after the aging treatment and the resistance increases evidently with increasing the W content. The higher extrinsic CFCG resistance in the aged microstructure is attributed to the roughness-induced crack closure, due to the brittle fatigue failure along the precipitation-weakened grain boundaries. The intrinsic CFCG resistance mainly results from the decrease in the corrosion rate by moderating the Cr depletion due to the addition of W that suppresses the precipitation of σ phase.