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Fundamentals of High Temperature Processes**Calcium and magnesium deoxidation in Fe-Ni and Fe-Cr alloys equilibrated with CaO-Al₂O₃ and CaO-Al₂O₃-MgO slags**H. OHTA *et al.*

Calcium and magnesium deoxidation equilibria in Fe-20 to 60mass%Ni, Fe-10 to 40mass%Cr and Fe-18mass%Cr and 8mass% Ni alloys saturated with CaO-Al₂O₃ and CaO-Al₂O₃-MgO slags have been studied at 1873 K using CaO, Al₂O₃ and MgO crucibles. Based on these results, the interaction coefficients between Ca and O and between Mg and O are estimated for Fe-Ni, Fe-Cr and Fe-Ni-Cr alloys. The solubilities of CaO and MgO calculated by using these interaction coefficients are compared with the observed values. The phase stability regions in the Fe-40mass%Ni-Al-O-M and Fe-20mass%Cr-Al-O-M (M=Ca and Mg) systems are presented at 1873 K.

(cf. *ISIJ Int.*, **43** (2003), 1293)**Thermodynamics of aluminum and manganese deoxidation equilibria in Fe-Ni and Fe-Cr alloys**H. OHTA *et al.*

Aluminum deoxidation equilibrium and manganese distribution have been studied at 1873 K in the equilibrium experiment between CaO-Al₂O₃ slags and Fe-10, 20, 40 and 60mass%Ni alloys or Fe-10, 20 and 40mass%Cr alloys containing Mn and Al. On the basis of these results, the effect of Ni or Cr on the activity coefficients of Al and Mn based on liquid iron is discussed and the interaction coefficient between Al and O in liquid iron has been estimated. Some experiments in which Fe-18mass%Cr-8mass%Ni alloy containing Al and Mn was equilibrated with CaO-Al₂O₃ slags have been carried out at 1873 K. It was found that the observed values for the oxygen content and the Mn distribution ratio in Fe-18mass%Cr-8 mass%Ni alloy are in good agreement with the calculated values by using the activity coefficients of Al and Mn obtained in this study.

(cf. *ISIJ Int.*, **43** (2003), 1301)**Kinetic study of factors affecting *in situ* reduction of silica in carbon-silica mixtures for refractories**V. SAHAJWALLA *et al.*

We report a systematic investigation on *in situ* reduction kinetics of silica in carbon based materials for refractories as a function of system parameters. The objective of this fundamental study was to establish factors influencing gasification of refractories, which in turn could lead to carbon depletion and refractory degradation. Experiments were carried out on silica-graphite mixtures for refractory applications as a function of temperature, compacting pressure, carrier gas flow rate, and additional oxides. The off gases (CO, CO₂) generated from silica reduction and carbon oxidation processes were analysed using an infrared detector to estimate overall reaction rate constants. Additional oxides such as Al₂O₃ and ZrO₂, had a significant effect on the reduction kinetics. The rate of SiO₂ reduction was

found to be mixed controlled by chemical reaction and mass transfer. Overall activation energy of bulk reactions taking place in the silica-graphite mixtures during initial stages of contact was estimated to be 153 kJ/mol.

(cf. *ISIJ Int.*, **43** (2003), 1309)**Reduction of titania-ferrous ore by carbon monoxide**E. PARK *et al.*

The reduction of titania-ferrous ore (ironsand) containing 57.2 wt% of iron and 7-8 wt% of TiO₂ was investigated in non-isothermal and isothermal reduction experiments using CO-CO₂-Ar gas mixtures in a laboratory fixed bed reactor. Samples in the course of reduction were characterised using XRD, EPMA and SEM.

Two types of particles were identified in ironsand: 1) homogeneous particles of titano-magnetite with cubic spinel structure (a major type); and 2) non-homogeneous particles, characterised by lamellar structure of rhombohedral titano-hematite, exsolved from the titano-magnetite.

Titano-magnetite, which is a magnetite-ulvospinel solid solution (Fe₃O₃)_{1-x}(Fe₂TiO₄)_x, with $x=0.27\pm 0.02$, was reduced to metallic iron and titanium sub-oxides. Titanium had a strong effect on the mechanism and rate of reduction of iron oxide in ironsand.

(cf. *ISIJ Int.*, **43** (2003), 1316)**Control of reverse emulsification and mixing time in a bottom blown bath covered with top slag**S. YAMASHITA *et al.*

Water model experiments were carried out to seek a possibility to control reverse emulsification, *i.e.*, entrapment of slag droplets and mixing time in the molten metal layer covered with top slag. The bath was agitated by centric bottom gas injection. A circular plate was immersed in the bath to change the flow pattern. When the diameter of the plate was larger than the width of the bubble dispersion region formed above the centric nozzle, the recirculating flow was significantly strengthened. As a result, the reverse emulsification and mixing time were systematically controlled by moving the plate in the vertical direction.

(cf. *ISIJ Int.*, **43** (2003), 1326)**The modeling of the gas flow and its influence on the scale accumulation in the steel slab pusher-type reheating furnace**Y. TANG *et al.*

The gas flow in the pusher-type reheating furnace coupled with fluid dynamics, combustion and radiation was modeled in this work. CFD Simulation results described a detailed flow distribution in the steel reheating furnace and indicated a reverse flow existing under the slab near the burners in the lower heating zone. This reverse flow could be the main reason for the scales accumulation in the front part of the heating zone. The oxygen distribution in the furnace was also calculated and the mass fraction is about 4%. The oxygen distributes uniformly inside

the most parts of the furnace except the areas near the burners.

(cf. *ISIJ Int.*, **43** (2003), 1333)**Model experiment on the dispersion of fine particles in a molten metal bath agitated by plunging jet**K. ABE *et al.*

Cold model experiments were carried out to understand the dispersion of particles introduced into a water bath and a mercury bath by a plunging jet. The particles were uniformly dispersed in the whole bath in a short time regardless of the density and diameter of the particles under the conditions considered. The results imply that small particles can also be uniformly dispersed in molten steel baths by using a plunging jet. Two time scales were introduced to characterize the dispersion of particles. One is time for the plunging jet to reach the bottom wall of the vessel. The other is time for the particles to uniformly disperse in the whole bath. Empirical equations for the two time scales were derived.

(cf. *ISIJ Int.*, **43** (2003), 1342)**Wetting of solid Al₂O₃ with molten CaO-Al₂O₃-SiO₂**J. Y. CHOI *et al.*

The wetting behavior of solid Al₂O₃ with molten CaO-Al₂O₃-SiO₂ was investigated at 1873 K using the sessile drop method. A new model was developed to represent the time dependence of the contact angle, *i.e.*, the spreading behavior of a liquid drop on a solid substrate. The model takes into consideration chemical interactions which continually take place at the interface between the solid Al₂O₃ and molten CaO-Al₂O₃-SiO₂. By applying the model to the experimental results of the present study the equilibrium contact angle between the liquid slag and solid alumina was determined for a number of different slag compositions, and an iso-contact angle diagram was constructed. The equilibrium contact angle was greatly affected by the slag composition, and it was found that the interfacial tension was the major factor governing the equilibrium contact angle. In the region of low SiO₂ content, the slag with higher CaO content exhibits a smaller contact angle, *i.e.*, better wettability with alumina. For slag with a given CaO/SiO₂ ratio, an increase in Al₂O₃ results in a corresponding increase in the contact angle, *i.e.*, decrease in wettability. For a given CaO/Al₂O₃ ratio, the variation of the contact angle with SiO₂ content shows a minimum. The contact angle decreases by increasing the surface roughness of the alumina substrate.

(cf. *ISIJ Int.*, **43** (2003), 1348)**Vapor pressure measurement of zinc oxychloride**S. H. SON *et al.*

The vapor pressures of ZnCl₂ at high oxygen partial pressure were measured by transpiration method at 823 K and 873 K. The vapor pressures of ZnCl₂ decreased with increase of the oxygen partial pressure. The oxygen content in ZnCl₂ melt and the

chlorine partial pressure in the system increased with increasing the oxygen partial pressure. These results indicate that the activities of $ZnCl_2$ melt are changed by the formation of zinc oxychloride in the melt at high oxygen partial pressure. The formation reaction of zinc oxychloride in the melt is suggested by the reaction $ZnCl_2(l) + 1/2 O_2(g) = ZnOCl(l) + 1/2 Cl_2(g)$. From the oxygen contents in the $ZnCl_2$ melt and the vapor pressure of $ZnCl_2$, the activities of $ZnCl_2$ in the $ZnCl_2$ - ZnO system are calculated. The activities of $ZnCl_2$ in the system show a negative deviation from Raoult's law.

(cf. *ISIJ Int.*, **43** (2003), 1356)

Transient flow analysis of stratified two liquid layers contained in rotating cylindrical vessel

T.YAMAGUCHI et al.

Experimental and numerical investigations were carried out on the transient behaviors of stratified two liquid layers contained in a cylindrical vessel suddenly set in rotation. Particular attention was paid to the deformation of the free surface and that of the interface between the two liquid layers. This flow field is a primary model for the formation of a plume eye on the surface of a bottom blown bath covered with a top slag layer. The numerical result could satisfactorily predict the time-dependent contours of the free surface and the interface. This mathematical model is also useful for the prediction of the interfacial area between molten metal and slag in a promising novel refining process using a suddenly rotating cylindrical vessel.

(cf. *ISIJ Int.*, **43** (2003), 1362)

Ironmaking

Abnormal swelling during reduction of binder bonded iron ore pellets with CO-CO₂ gas mixtures

S.HAYASHI et al.

Abnormal swelling during reduction of iron ore pellets with CO-CO₂ gas mixtures was investigated in the temperature range of 700 to 1 000°C.

Influence of addition of gaseous sulfur COS at low partial pressures to inlet gas mixtures, CO₂/(CO+CO₂) in inlet gas and temperature as well as kinds of binders such as Portland cement, bentonite and lime on swelling were examined.

When the ratio P_{COS}/P_{CO} in inlet reducing gas was lower in 10^{-2} than the equilibrium ratio between iron and iron sulfide, abnormal swelling of pellets was observed for non cement bonded pellets, in particular, giving maximum around 900°C. Cement bonded pellets provided moderate abnormal swelling independently of adding gaseous sulfur to inlet gas mixtures. Their swelling seemed to be caused by gasification of sulfur species present in cement. These results supported our previous findings that the existence of sulfur is essential to the abnormal swelling and the swelling is mostly accompanied with the formation of fibrous irons.

The results are discussed along with previous researches and gas chromatography of sulfur species in exit gas to evaluate the sulfur activity in gas near the reaction front inside cement bonded pellets.

(cf. *ISIJ Int.*, **43** (2003), 1370)

Behavior of stress field in packed bed of kokura No. 2 blast furnace during filling and after blow-in

T.INADA et al.

As the first trial in the world, the stress field in Kokura No. 2 Blast Furnace during filling and after blow-in was measured. The characteristics of transitional behavior of the measured stress field is as follows: 1) In filling process, the vertical stress at the tuyere level increased with amount of charged burden, but the rate of increase gradually dulls. 2) The high stress was observed at the central part of the furnace in comparison to the intermediate. 3) After descent occurred by the blast start, the vertical stress remarkably increased at the furnace center. 4) The origin of the change of stress field appears to be located at tuyere region as a sink of burden and the change propagates toward the furnace center.

The simulation based on elasto-plastic theory reproduces the measured value well, and the validity of the simulation method was confirmed. By use of the simulation method, the mechanism of the transitional change in stress field after blow-in is also discussed. Before blow-in, the region in passive state is not found in the furnace, and the yield region appears a little at peripheral part of the upper shaft and belly. As the descent occurs, the arched field of stress is formed above tuyere, and one end of the arch is located at the bosh wall, and the other end heads for the furnace center, *i.e.* deadman. The remarkable increase of the vertical stress at the furnace center after blow-in is supposed to be induced by the growth of the arch.

(cf. *ISIJ Int.*, **43** (2003), 1376)

Influence of iron ore characteristics on penetrating behavior of melt into ore layer

J.OKAZAKI et al.

It is important to maintain a certain amount of melt during sintering of iron ores to improve product yield and strength of sinter product. Spreading phenomena of the initial melt within adhering layer in pseudo-particles are essential to achieve efficient agglomeration. Penetration tests have been conducted to demonstrate the spreading behavior of the initial melt. Paired samples consisting of ore tablet and initial melt tablet were heated and penetration length was measured. Penetration behavior of melt during sintering was discussed on a base of capillarity. Determining factors of penetration were morphology of the ore surface before and after dehydration and chemical composition of ores. Product yield and the strength of sinter were reflected by the penetration length of blended ores in a sintering plant.

(cf. *ISIJ Int.*, **43** (2003), 1384)

Factors influencing the Bonding phase structure of iron ore sinters

C.E.LOO et al.

The properties of melts formed in the flame front during iron ore sintering determine the structure of the ensuing sinter bonding phases. The tumble strength of sinter particles and yield from a sinter strand are largely determined by the inherent strength and structure of the bonding phases pre-

sent. In this study, bench-scale tests were carried out to study the effect of melt chemical composition and sintering conditions on bonding phase micro-structure. The study showed that phosphorus, silica, alumina and magnesia levels, sinter basicity and maximum sintering temperature influenced bonding phase structure through the reshaping and coalescing of the melt and bubbles. Information in the literature indicates that some of the observed changes in pore properties can be explained by changes in viscosity and surface tension of the melts. The inability to explain all the changes are most likely related to the differences in chemical compositions between melts considered in the literature and the sintering melts formed in this study. The study also showed that image analysis could be used to provide a reliable objective description of the obtained sinter micro-structures.

(cf. *ISIJ Int.*, **43** (2003), 1393)

Steelmaking

A new numerical model for predicting carbon concentration during RH degassing treatment

Y.-G.PARK et al.

A new decarburization model for the RH system was constructed to calculate the decarburization reaction using a three-dimensional fluid dynamics program. The behavior of Ar gas and the entire fluid flow in the RH process were considered. On the basis of this fluid flow, the decarburization reaction could be calculated by establishing the decarburization reaction model, which considers thermodynamics, reaction kinetics, and the decarburization sites (Ar bubble surface, bath surface, and the CO bubble formation at inner sites). The model showed good agreement with two RH operation results. Using this numerical model, the contributions of each reaction were investigated.

(cf. *ISIJ Int.*, **43** (2003), 1403)

Effect of nozzle twisted lance on jet behavior and spitting rate in top blown process

Y.HIGUCHI et al.

It is important to well-design the shape of lance nozzle to suppress the spitting phenomena in top blown process such as a converter. Normal lance in which axes of lance and nozzles intersect one another has been used in spite of its limitations conventionally.

In the present work, 6 nozzle lances with twisted nozzles in which axes of lance and nozzles have no points in common were newly designed and the effects on the spitting behavior and the characteristics of jets were investigated by cold model experiments.

"Nozzle twisted lance" showed a lower spitting rate at the optimum twist angles of 11.4 degrees which was lower than that of normal lance. Jet behaviors were also different from those of the normal lances and changed according to the twist angle. Suppression effect of "nozzle twisted lance" on the spitting rate could be partially explained by an increase of the shift of the jet pressure from the lance axis.

(cf. *ISIJ Int.*, **43** (2003), 1410)

Casting and Solidification

Origin of equiaxed grains and their motion in the liquid phase

H.ESAKA *et al.*

In order to investigate the multiplication of equiaxed grains by the forced convection, *in-situ* observation using a transparent organic substance have been made. The emission of some spherical particles from the columnar zone was observed by a fiber scope installed in an ingot case. These particles are originally the secondary dendrite arms and are detached by the fluctuations of thermal and/or solutal fields and/or mechanical breaking. Then the particles fell down in the liquid along with the natural convection. This event has taken place approximately 30 s before the well-developed equiaxed grains started to form. Therefore, these particles developed to equiaxed dendrites floating around in the liquid.

A physical model for formation of equiaxed grains based on the observation has been proposed. The experimental results on the change in multiplication rate with time could be reasonably explained by this physical model.

(cf. *ISIJ Int.*, **43** (2003), 1415)

Forming Processing and Thermomechanical Treatment

Computational exploration of microstructural evolution in a medium C–Mn steel and applications to rod mill

P.A.MANO HAR *et al.*

An 'Expert System' is proposed in this work to conduct computational exploration of the deformation and restoration behaviour of a medium C–Mn steel under high strain rate conditions, at elevated temperatures and complex strain paths that occur in rod rolling process. The expert system computes appropriate thermomechanical parameters necessary for describing rod rolling process in detail and then utilizes these parameters in mathematical models to determine microstructure evolution during a typical industrial-scale rod rolling process. Microstructure simulation in rod rolling is a challenging problem due to the fact that several softening processes may operate sequentially or concurrently during each deformation step. Different softening processes have very different impact on microstructure development and therefore it is important to investigate the particular combinations of processing conditions under which transition of operating softening processes occurs. In the present work, the transition from dynamic to metadynamic recrystallization is studied in detail based on the criteria of critical strain, austenite grain size and Zener–Hollomon parameter when the interpass (interdeformation) time is very short of the order of few milliseconds during the later stages of rod rolling. Computational results are subsequently validated by comparing the program output to in-plant measured microstructure data. The proposed expert system is designed as an off-line simulation tool to examine and assess the various options for thermomechanical process optimization.

Transformations and Microstructures

Precipitate dissolution and grain growth in the heat affected zone of HSLA-100 steel

M.SHOME *et al.*

An attempt has been made to predict the dissolution of Nb(CN) precipitates in the heat affected zone (HAZ) of a Nb containing HSLA-100 steel. An invariant size approximation model along with existing solubility product data have been applied to continuous heating and cooling situation to ascertain the kinetic strengths from heat input–peak temperature conditions at which dissolution of precipitates take place. Peak temperatures beyond which precipitates rapidly dissolve and cause grain growth have been identified, and they are in consonance with the austenite grain growth data.

(cf. *ISIJ Int.*, **43** (2003), 1431)

Effect of Co addition on microstructure in high Cr ferritic steels

K.YAMADA *et al.*

Co is one of the interesting alloying elements in advanced high Cr ferritic steels used to improve their creep properties at elevated temperatures. However, it has been reported that Co bearing tends toward rapid deterioration in creep property at long-term testing. In this study, microstructures were studied in detail by comparing two kinds of 9% Cr ferritic steels with 3% Co and Co free for better understanding difference in those creep behaviors.

Creep property of the steel with 3% Co was superior to that of the steel without Co within this study, as many researchers pointed out. Adding Co certainly suppressed δ -ferrite formation and there was large difference in prior-austenite grain size between two steels after tempering. In addition to this macroscopic difference, there was also remarkable change in precipitation behavior between them. It was found that heterogeneous precipitation of inter-metallic compounds and MX type carbonitrides was observed in Co free steel, while any extreme localization of such precipitation were not seen in 3% Co steel.

It was deduced that such microstructural difference in connection with δ -ferrite formation between two steels was an important factor to understand better high temperature creep properties in 3% Co steel rather than those in Co free steel.

(cf. *ISIJ Int.*, **43** (2003), 1438)

Orientation selective martensite transformation in an Fe–28Ni alloy

L.KESTENS *et al.*

A variant selection phenomenon was studied during the phase transformation in an Fe–28%Ni alloy, which was slowly cooled to room temperature at a rate of 1°C/min after reheating to 1000°C, or warm rolled at ~250°C during air cooling. The textures of parent and product phases were determined on the basis of local orientation measurements in the austenite and martensite phase. The measured product textures were compared with the modeled ones, which were obtained by applying the Bain, Kurdju-

mov–Sachs and Nishiyama–Wassermann transformation laws on the local austenite grains. It was shown that the presence of a deformation substructure is not an essential prerequisite for the occurrence of variant selection. The data reveal that a variant selection mechanism is active also in not deformed samples, containing a fully recrystallized parent matrix. The nature of the variant selection mechanism is discussed in terms of the elastic anisotropy of the parent phase.

Mechanical Properties

Quantitative analysis of three-dimensional fatigue fracture surface reconstructed by stereo matching method

M.TANAKA *et al.*

Three-dimensional geometry of a fatigue fracture surface in a Cu–Be alloy (the grain diameter is about 24 μm) was reconstructed by the stereo matching method based on the coarse-to-fine method. The fractal dimensions of the contours and of the fracture surface profiles extracted from the reconstructed image were then estimated by the box-counting method in the scale length range smaller than about one grain-boundary length (about 14 μm). The mean value of the fractal dimension of the contours was about 1.238, and was close to that of the actual fracture surface profiles in the plane in parallel with the crack growth direction (about 1.210) (in the parallel direction) and in the plane perpendicular to the crack growth direction (about 1.190) (in the perpendicular direction). Thus, the stereo matching method can reproduce the three-dimensional image of the complex fracture surface. However, the mean value of the fractal dimension of the reconstructed fracture surface profiles (about 1.128 in the parallel direction and about 1.146 in the perpendicular direction) was a little smaller than that of the actual fracture surface profiles, since there were microstructural features such as overhang, debris and microcracks on the fatigue fracture surface, which were only partly reproducible by the stereo matching method. Nevertheless, the geometrical information about a given fracture surface in a wide area can be obtained by the three-dimensional fracture surface reconstruction and analysis. Combination of three-dimensional and two-dimensional analyses may lead to the further understanding of the geometrical features of fracture surfaces and the fracture mechanism in materials. The fractal dimension was found to be a useful index not only for characterizing fracture surfaces but also for comparison of the result of three-dimensional image reconstruction with the actual fracture surface morphology.

(cf. *ISIJ Int.*, **43** (2003), 1453)

Social and Environmental Engineering

Effects of steelmaking slag addition on growth of marine phytoplankton

K.HARAGUCHI *et al.*

Culture experiments of a natural phytoplankton assemblage collected from coastal surface water and

a mono-specifically cultured diatom were conducted to investigate the possibility of steelmaking slags to use as a nutrient resource for marine phytoplankton. Two kinds of slags, a decarburization slag and a dephosphorous slag, were tested in batch cultures under freely drifting pH. Leaching experiment to determine dissolution of nutrient elements from the slags demonstrated that phosphate and reactive silicate are released into seawater, while rate of their dissolutions does not simply depend on amount of

the slags. Excess addition of the slags (3 300 mg/l) decreased phosphate in the seawater probably due to precipitation with calcium of main component of the slags. Growth of natural phytoplankton assemblage was evidently enhanced by addition of the slags at 33 mg/l. However, excess addition (3 300 mg/l) suppressed the growth of phytoplankton due to not only decreased phosphate and silicate but also increased pH to 10. This shift to alkaline might decrease considerably solubility of iron (es-

sential nutrient for phytoplankton growth) although organic ligands existed. These results indicate that slag enrichment would be effective at lower dose to avoid pH increase. Although in our study 33 mg/l was confirmed to be the best dose, solubility of the elements and pH increase might be different with different slags. Therefore, the best dose should be determined for each slag before application.

(cf. *ISIJ Int.*, **43** (2003), 1461)