

Fundamentals of High Temperature Processes

Liquid solution thermodynamics in the alumina-saturated Fe-C-Pb system

S. MALHOTRA *et al.*

The solubility of molten lead in alumina-saturated molten iron-carbon alloys was determined as a function of temperature and carbon content. Lead solubility in these melts decreases with decreasing temperature and carbon content. The results were applied to the unified interaction parameter formalisms of Bale and Pelton to develop expressions for predicting lead solubility in this system as a function of temperature and composition.

Oxidation-reduction equilibrium of manganese in CaO-Mn₂O-SiO₂ slags

AHMAD SOBANDI *et al.*

The oxidation-reduction equilibrium of manganese in the CaO-Mn₂O-SiO₂(-MgO-Al₂O₃) slag system has been investigated as functions of slag composition, oxygen partial pressure and temperature.

In the range of oxygen partial pressure of 3.04 to 21.28 kPa and temperature of 1 573 to 1 673 K, the (%Mn³⁺)/(%Mn²⁺) ratio was determined and expressed by the following equation:

$$\begin{aligned} \log (\% \text{Mn}^{3+}) / (\% \text{Mn}^{2+}) &= 0.86\{(\% \text{CaO}) + (\% \text{MgO}) + 0.436(\% \text{Mn}_2\text{O}) \\ &+ 0.126(\% \text{Al}_2\text{O}_3)\} / (\% \text{SiO}_2) \\ &+ 0.22 \log P_{\text{O}_2} (\text{Pa}) + 2860 / T - 4.44 \end{aligned}$$

The value of standard enthalpy change for the oxidation of Mn²⁺ to Mn³⁺ was determined to be -55 kJ/mol. The manganite capacity, C_{MnOx}, has also been arranged as a function of slag composition and temperature. Furthermore, on the basis of the present experimental data, the values of optical basicity of component oxides were estimated and compared with those reported by the other investigators.

Ironmaking and Reduction

Effects of metallic iron bearing resources on iron ore sintering

M. NAKANO *et al.*

In order to clarify the effects of the use of resources containing metallic iron (MIRs) on the sintering process, plant tests have been conducted at Nakayama Steel. With an increase in MIRs, the following results were observed:

- (1) Sinter yield and productivity deteriorated
- (2) Emissions of NO_x and SO_x were reduced
- (3) Sinter qualities changed depending on the kind of MIR

Pressure measurements of the sinter bed and CT observations of sintercake revealed that a decrease in porosity in the lower part of sintercake caused a decrease in permeability of the

bed and an increase in the volume of an unsintered portion near the hearth layer. A decrease in fuel nitrogen and sulfur inputs in the sinter mix, which was caused by substituting metallic iron for coke breeze, reduced the emissions of NO_x and SO_x.

Use of waste lubricant oil from steel rolling mills in the coking process

R. ALVAREZ *et al.*

The main objectives of this research have been to study the possibilities of using residual oils from the steel rolling mill process as an additive in a coal blend to be carbonized in a coke oven plant and, consequently, to reduce the cost of coking blends. This type of residual oils is classified as a hazardous material difficult to get rid of.

Previous to the addition to a coking blend, waste oil from the rolling-mill process (tinnol) was treated to remove iron dust materials and reduce water content. Afterwards it was added to coking charges, using an installation specially designed for heating, transport and the pulverization of such oils.

The influence of these oil additions on the coking process and coke quality has been studied, using the 250 kg movable wall and the 6 t ovens of the INCAR Experimental Coking Test Plant. A possible method of recycling these waste oils within the coking process has been found, backed by tests carried out to pilot and semi-industrial scale.

Infiltration of metallurgical coke by pyrolysis of CH₄ and its effect on enhancement of CSR

Y. SHIGENO *et al.*

Metallurgical coke was modified by infiltrating carbon within the pores by methane pyrolysis. The rate of oxidation with CO₂ was lowered and the mechanical strength after partial oxidation was enhanced. CSR(Coke Strength after CO₂ Reaction) of regular coke for a blast furnace increased from about 56 to 77. This enhanced value corresponds to that of the extremely high-grade coke. The mechanism was considered in terms of the pore structure changes and was elucidated as follows:

Original metallurgical coke has a negligibly small volume of micropores but it increases rapidly during oxidation. In the case of infiltration, carbon deposits in the mesopores. This carbon restricts the rapid increase in the volume of the micropores during oxidation, which is attributed to depress the oxidation rate. As it has been realized that generally the coke with the higher resistance to oxidation has the higher CSR, the depression effect onto the oxidation rate is deduced to result in the extreme enhancement of CSR.

Steelmaking and Refining

Effects of additives in BaO-BaF₂-MnO slag on phosphate and manganese capacities

X. LIU *et al.*

The effects of various additives (CaO, MgO, SiO₂, CaF₂ and Al₂O₃) in BaO-BaF₂-MnO slags on the distribution ratios of phosphorus and manganese between the slags and ferro manganese have been studied at 1300°C. The dephosphorization ability of BaO-BaCl₂-MnO slags is also investigated. It is found that replacement of BaO with CaO or MgO causes a decrease in the phosphate capacity and an increase in the manganese capacity, and that substitution of BaF₂ with CaF₂ or SiO₂ results in a poor dephosphorizing ability and more losses of manganese from metal to slags. CaF₂ in BaO-BaF₂-MnO slags strongly reduces the BaO activity, which diminishes the beneficial action of BaO in the slags on dephosphorization. Comparing with BaO-BaCl₂-MnO slags, BaO-BaF₂-MnO slags give a higher dephosphorizing capacity. Critical contents of different additives in BaO-BaF₂-MnO slags to achieve an effective dephosphorization have been given.

Based on the fact that the relationships between optical basicity and the phosphate and manganese capacities are only valid in a restricted range of slag compositions, the relationships between the capacities and optical basicity and slag composition have been derived by considering the interaction of slag components and analyzing a host of experimental data from different authors. These relationships are expected to be useable in a wider range of slag compositions and temperatures and to predict the phosphorus and manganese contents in metal without serious error.

Casting and Solidification

Characteristics of oxide precipitation and growth during solidification of deoxidized steel

Z. MA *et al.*

With the help of thermodynamics and kinetics, the oxide metallurgy with respect to Ti treatment of low carbon steels is theoretically analysed. It is attempted to define and predict the optimal conditions for deoxidation of molten steel, which are decisive factors for controlling secondary inclusions, using the analysing method described below. The composition and growth of oxides during solidification are obtained by calculation featuring a good agreement with reported experimental results. But the present analysing model needs to be further modified in view of deoxidation kinetics.

Analysis of mold wear during continuous casting of slab

Y.M. WON *et al.*

Using a 2-dimensional coupled thermo-elasto-plastic finite element model, the thermo-mechanical behaviours of the strand and mold were analyzed. The calculated geometry and temperature distributions of the solidifying shell and mold were compared with experimental observations. The calculated geometry around corner region was in good agreement with experimental observations. The mold wear was analyzed by a new dimensionless parameter of "Apparent Wear Parameter" which is inversely proportional to yield stress of the mold at service temperature and directly proportional to the interfacial pressure between the strand and mold. The effects of narrow face taper and carbon concentration of cast steel on mold wear were analyzed using the apparent wear parameter. With increasing narrow face taper, the possibility of mold wear increased due to increasing interfacial pressure. With increasing carbon concentration, the width of worn region of 35 mm at 0.05 and 0.1 wt% C steels decreased to 15 mm of 0.2 wt% C steel due to uniform thermal contraction of 0.2 wt% C steel during solidification. The calculated behaviours of mold wear were compared with used mold in industrial operation. The calculated worn region of mold based on the apparent wear parameter were in good agreement with industrial observations.

Three-dimensional simulation of dendritic grain structures of gas-atomized Al-Cu alloy droplets

Y.H. CHANG *et al.*

A three dimensional stochastic model was developed for the prediction of dendritic grain structures of gas atomized Al-Cu droplets in a non-uniform temperature situation. The present model was based on a three dimensional Cellular Automaton (CA) technique coupled with the Finite Volume (FV) heat flow calculation. The physical system was divided into uniform cubic CA Cells which were characterized by growth orientation, temperature and physical states. The LKT(Lipton-Kurz-Trivedi) model was adopted to evaluate the growth kinetics of a dendrite tip. The effects of the process variables, such as the amount of undercooling, the size of droplets and the heat transfer coefficient on the formation of the grain structures of atomized Al-Cu droplets were investigated. The calculated solidification grain structures were in good agreement with those obtained experimentally. It was found that the present model can be used to predict the formation of solidification grain structures in rapid solidification under non-uniform temperature conditions.

Prediction of the δ to γ transition in austenitic stainless steels during laser treatment

S. FUKUMOTO *et al.*

Laser remelting experiments have been performed with austenitic stainless steels to evaluate the effects of composition (Cr/Ni-equivalent between 1.52 and 1.61) and solidification velocity ($V_s=1$ to 30 mm/s) on the phase selection between primary δ -ferrite and primary γ -austenite. Experimental results were compared with previous work. The Cr/Ni-equivalent is useful to predict the transition from δ to γ by comparison with microstructural transitions in the Fe-Cr-Ni ternary system. The δ to γ transitions can be modeled by the dendrite growth theory for multicomponent systems. The calculated results show the potential of this approach for the analysis of microstructure formation.

Microstructure

Role of in-grain shear bands in the nucleation of $\langle 111 \rangle$ ND recrystallization textures in warm rolled steel

M.R. BARNETT

Electron Back Scattering Diffraction (EBSD) analysis was carried out on warm rolled Ti-IF and low carbon (LC) steels. The aim of this study was to learn more about the formation of grains with a $\langle 111 \rangle$ axis parallel to the sheet normal (ND fibre grains) during annealing. In-grain shear bands were found to be more prevalent in the deformed microstructure of the IF steel than in that of the LC grade. Consequently, the deformed ND fibre grains were far more fragmented in the IF material. These fragmented ND fibre grains produced ND fibre oriented nuclei in the grain interiors during annealing. It is concluded that the relative absence of in-grain shear banding in the warm rolled ELC material is the most likely reason for the absence of an ND fibre recrystallization texture in this steel. It is also postulated that in-grain shear bands are involved in the nucleation of the near $\{554\} \langle 225 \rangle$ textures that are often observed in cold rolled and annealed IF and ELC product.

Evaluation of driving force and mobility for diffusion induced grain boundary migration in Ni(Cu) system

M. MORIYAMA *et al.*

The kinetics of diffusion induced grain boundary migration (DIGM) in the Ni(Cu) system was experimentally studied by Liu *et al.* using polycrystalline Cu/Ni/Cu diffusion couples annealed at 888 K for various times between 4.8×10^2 and 9.36×10^4 s. The notation Ni(Cu) means that Cu atoms diffuse into a pure Ni or binary Ni-Cu phase. Their experimental results have been quantitatively analyzed

using the energy balance model proposed by Kajihara and Gust. The face-centered-cubic (f.c.c.) solution phase in the binary Ni-Cu system is assumed to be elastically isotropic. The molar Gibbs energy of the f.c.c. phase is expressed by a subregular solution model. The migration rate v of the moving grain boundary is described as a function of the reaction time t by the equation $v = k(t/t_0)^m$. Here, t_0 is unit time, 1 s. From these relationships, the effective driving force $\Delta^e G_m$ for DIGM has been calculated as a function of the reaction time. Although $\Delta^e G_m$ monotonically decreases with increasing reaction time from the maximum value of 184 J/mol to the minimum value of 8 J/mol, it is still large enough to drive the grain boundary migration against the curvature of the moving grain boundary even at late stages of the reaction. The mobility M of the moving grain boundary also monotonically decreases with increasing reaction time from 2×10^{-17} m⁴/Js at 4.8×10^2 s to 2×10^{-18} m⁴/Js at 9.36×10^4 s. However, considering the grain boundary energy contribution due to the curvature of the moving grain boundary, M is supposed to be almost constant during the reaction.

Social and Environmental Engineering

Development of Cu/ZnO/Al₂O₃ catalyst for dimethyl ether synthesis from CO-CO₂-H₂ mixture

T. AKIYAMA *et al.*

The objective of this study is to develop a catalyst for direct synthesis of dimethyl ether ((CH₃)₂O, DME) from a CO-CO₂-H₂ mixture such as blast furnace gas. For this purpose, precipitated Cu-ZnO-X (X = Al₂O₃, Cr₂O₃, ZrO₂ or Ga₂O₃) were systematically prepared by changing chemical composition and their catalytic activity was measured. For Cu-ZnO-Al₂O₃ catalyst, compositional research was on two parameters, namely Cu/ZnO ratio (3/7~5/5) and content of Al₂O₃ (0~33.0 mol%). The influence of each parameter was estimated by DME and MeOH yields for the same catalyst mass. Some Cu-ZnO-Al₂O₃ catalysts synthesized DME more than MeOH, in which the DME activity was related to specific surface area and existence of broadened ZnO peaks in XRD patterns. In contrast, three other Cu-ZnO catalysts including another oxide (Cr₂O₃, ZrO₂ or Ga₂O₃) synthesized only MeOH without DME. Content of Al₂O₃ was more influential on DME synthesis than Cu/ZnO ratio. In conclusion, the most active composition of Cu-ZnO-Al₂O₃ catalyst for DME synthesis was Cu/ZnO=4/6 with 14.3 mol% Al₂O₃ and interestingly this composition was included within the range of usual MeOH synthesis catalysts.

Optimal operating conditions for the primary end of an integrated steel plant : genetic adaptive search and classical techniques

B.DEO et al.

The optimal operating conditions for the primary end of an integrated steel plant, which

essentially comprises of sintering plant, pelletizing plant, blast furnaces, oxygen steelmaking converters and electric arc furnace, are found through a modern technique of optimization, namely, genetic adaptive search (GAS), and also through classical techniques of simplex search with simulated annealing (ASM) and sequential quadratic programming (SQP). A

comparison of these techniques shows that GAS outperforms both the classical methods and obtains the lowest cost solution. Based on this study, it is recommended that GAS be used, in preference to other methods, in complex steel plant optimization problems.

お詫び

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