

## Fundamentals of High Temperature Processes

### Activity of phosphorus oxide in CaO–MnO–SiO<sub>2</sub>–PO<sub>2.5</sub>(–MgO, Fe<sub>2</sub>O) slags

A.SOBANDI *et al.*

The CaO–MnO–SiO<sub>2</sub>–PO<sub>2.5</sub>(–MgO, Fe<sub>2</sub>O) slags were equilibrated with liquid copper alloys in a molybdenum crucible under a flowing CO<sub>2</sub>/H<sub>2</sub> atmosphere in the temperature range of 1573 to 1673 K.

The activity coefficient of PO<sub>2.5</sub>,  $\gamma_{\text{PO}_{2.5}}$ , and the phosphate capacity,  $C_{\text{PO}_4} = (\% \text{PO}_4^{3-}) / p_{\text{P}_2}^{1/2} p_{\text{O}_2}^{3/4}$ , of the slags were expressed as follows:

$$\begin{aligned} \log \gamma_{\text{PO}_{2.5}} = & -2.59\{(\% \text{CaO}) + 0.33(\% \text{MnO}) \\ & + 0.55(\% \text{MgO}) - 0.90(\% \text{Fe}_2\text{O}) \\ & - 0.77(\% \text{PO}_{2.5})\} / (\% \text{SiO}_2) + 1400/T \\ & - 5.75 \end{aligned}$$

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The phosphorus distributions between hot metal and the slag were examined, based on the thermodynamic data obtained in the present study. From comparison with the plant data, it was concluded that the thermodynamic data obtained in the present study are satisfactorily applicable to the thermodynamic assessment of hot metal pretreatment with high MnO slag.

### Rates of evaporation in a vacuum in liquid Ni–Ti alloys

Y.OGASAWARA *et al.*

The activities in liquid Ni–Ti alloys were experimentally measured by the Langmuir vaporization method. By using measured rates of evaporation and temperatures, the activities of nickel and titanium were calculated by applying Hertz–Knudsen equation and a regular solution model. An electron beam vacuum furnace with a water cooled copper crucible was used for evaporation experiments to avoid contamination by oxygen and gaseous elements. Temperature was measured by two color optical pyrometer. The rates of evaporation in pure substances were measured to verify Hertz–Knudsen equation with the evaporation coefficient  $\alpha$  of unity. Rates of evaporation in Ni–Ti alloys were then measured. This system was assumed to be a regular solution. Consequently activities of nickel and titanium were calculated to be about 0.04 at 50 at% at 1773 K. The activities obtained in this study were ranged between those in two studies in literatures. Results of this study agree reasonably with those for Ni–Al alloys in literatures. This system exhibits strong negative deviations from ideality. Moreover it was shown the possibility of thermodynamic measurements for the other systems which contain high reactive elements.

### Determination of free energy of $\delta$ -ferrite/ $\gamma$ -austenite interphase boundary of low carbon steels by *in-situ* observation

H.YIN *et al.*

Phase transformations of  $\delta$ -ferrite/ $\gamma$ -austenite in low carbon steels containing 0.017 mass% phosphorus are observed *in-situ* by using a combination of confocal scanning laser microscope with infrared image furnace. Dihedral angles at triple points of one high energy  $\delta/\delta$  grain boundary and two incoherent  $\delta/\gamma$  interphase boundaries are measured by holding the sample at temperatures where  $\delta$ - and  $\gamma$ -phases co-exist in quasi-equilibrium. From the average value of observed dihedral angles, free energy of  $\gamma/\delta$  incoherent boundary for a steel with low sulfur content (0.007 mass%) is estimated to be 0.450 J/m<sup>2</sup> at *ca.* 1700 K. The effects of temperature and sulfur content on the dihedral angle and free energy of incoherent  $\delta/\gamma$  boundary are also discussed.

### Development of a laser optical sensor for measuring bubble characteristics in an oily liquid bath

M.IGUCHI *et al.*

Oily liquids such as silicone oil and normal pentane have been commonly used as the model for top slag to investigate the role of the top slag on the mixing in the bath of various refining processes. An electroresistivity probe is a powerful tool for measuring bubble characteristics in a bath filled with a liquid of high electrical conductivity and it is extensively used in water model experiments. Unfortunately, the electrical conductivity of oily liquids is very low, and accordingly, the electroresistivity probe loses its validity in oily liquid baths. Considering these circumstances, a two-channel laser optical sensor was developed to measure the bubble characteristics in oily liquid baths. Gas holdup, mean bubble rising velocity and mean bubble chord length were measured accurately, whereas measurement of bubble frequency was disturbed by Doppler signals originating from the bubble surface.

## Ironmaking and Reduction

### Microstrength characteristics of high ash coke

B.CHAKRABORTY *et al.*

Experiments were carried out to determine the microstrength of different high ash coke samples obtained from 2 and 250 kg ovens. Microstrength of coke is determined using small quantity of sample (50 ml) with small sample size (3–6 mm) and is an indicator of the inherent strength of the coke matter. The microstrength values obtained were then correlated with the ash, VM/reflectance and fluidity of the parent coal and also conventional strength indices of coke like M10 and CSR. The correlations obtained indicate that except in the case of very strong coke, correlation exists between microstrength, M10 and CSR values of coke.

## Casting and Solidification

### Macro–micro modeling of the dendritic microstructure of steel billets processed by continuous casting

J.M.CABRERA-MARRERO *et al.*

Operating data of a steel billet caster such as casting speed steel temperature and cooling conditions in the water spray zone are employed to predict dendritic microstructures of solidified steel. For that semi-empirical equations to calculate primary and secondary arm spacing were derived from uni-directional solidification experiments of steel samples with various compositions. When these equations are combined with a heat transfer model, which involves operating parameters of a caster, it is possible to predict dendritic microstructures, making possible micro-modeling from macro-processing data.

Experimental measurements of primary and secondary arm spacing in four commercial steels agreed acceptably well by the predictions performed using this approach. The knowledge of microstructure will allow to pursue predictions of microsegregation phenomena.

### Mechanical behavior at high temperature of a centrifugal-casting stainless steel

J.A.JIMÉNEZ *et al.*

Mechanical properties at high temperature of a centrifugally-cast stainless steel tube have been investigated by torsion tests. Microstructure and composition have been determined in different positions along the tube radius. Differences in the microstructure related to different solidification rates have been observed between the interior and exterior zones. Garofalo's equation has been calculated considering the results of torsion tests of samples obtained from both zones. A similar value for the activation energy and hyperbolic sinus exponent have been observed in both cases. However, a change in ductility and fracture stress between both zones has been found at temperatures above 1100°C.

### Swirling effect in immersion nozzle on flow and heat transport in billet continuous casting mold

S.YOKOYA *et al.*

A numerical analysis and water model study of the mold region of a continuous casting apparatus are performed with a novel injection concept using swirling flow in the pouring tube, to control the heat and mass transfer in the continuous casting mold.

As a result, the following results were found:

- (1) By changing swirl strength, it is easy to control the flow pattern as well as the direction of the flow.
- (2) Uniform velocity distribution can be obtained within a very short distance from the outlet of the nozzle.
- (3) Heat and mass transfer near the meniscus can be remarkably activated compared with a conventional straight type immersion nozzle without swirl.
- (4) Swirl helps the superheat in the melt dissipate.
- (5) Penetration depth of nozzle outlet flow is de-

creased remarkably by the application of swirling.

Those findings mentioned above are very useful to control the flow pattern in the billet and bloom continuous casters.

### Heat transfer across mold flux film in mold during initial solidification in continuous casting of steel

*J.W. CHO et al.*

Analysis of heat transfer near the meniscus in mold for continuous casting of steel has been carried out by taking into account conductive and radiative thermal resistances of infiltrated mold flux film and thermal resistance at the copper mold/solidifying mold flux film interface. Mold fluxes in commercial use for casting low and medium carbon steel are selected for this study. Thermal conductivities, absorption coefficients and interfacial thermal resistances of these fluxes have been determined in our previous work by laser flash method, high temperature cell FTIR test and contacting thermal resistance test, respectively. Calculation with these data shows that the heat transfer is strongly influenced by the interfacial thermal resistance. Slow cooling required for casting surface crack sensitive medium carbon peritectic steel slabs can be achieved by making the interfacial thermal resistance high, which is attainable by use of basic mold fluxes with high rate of crystallization. A flux film thicker than 0.25 mm for the low carbon steel or 0.4 mm for the medium carbon steel is also found to be a requisite to prevent the occurrence of longitudinal surface cracks. Reasonably high interfacial thermal resistance and a proper flux film thickness are essential to reduce the surface defects and to increase the speed of continuous casting of these steel slabs.

### Water model study on convection pattern of molten steel flow in continuous casting tundish

*D.-Y. SHENG et al.*

Natural convection will obviously influence the liquid steel flow in continuous casting (CC) tundish, which cannot be neglected in tundish metallurgical process. Through the theoretical analysis, the dimensionless number,  $Gr/Re^2$ , is adopted to determine the convection pattern in tundish system. Validity of this criteria in a reduced scale water model are also discussed in this paper. Non-isothermal water model experiment with the temperature variation of inlet stream, has been simulated to see the effect of temperature variation of ladle stream. The convection pattern of molten steel flow in continuous casting tundish is also studied numerically by using the commercialized computational fluid dynamic (CFD) software package, CFX4. From the results of theoretical analysis, physical and mathematical model simulation, it can be stated that the convection pattern of molten steel flow in tundish is controlled by the combined nature convection and forced convection.

### Benefits, challenges and limits in new routes for hot strip production

*K. SCHWERDTFEGER*

In this lecture several aspects of the new casting

processes and of the linkage of casting with hot rolling into a combined in-line process is treated. A very important point is productivity. In a process with stationary mold the casting rate is limited by two phenomena, namely rate of shell growth and friction between strand and mold. Model computations show that the maximum casting rate for secure casting is in the range of 5 to 10 m min<sup>-1</sup>. In the new strip casting processes with traveling molds in which the friction problem does not arise the productivity may be constrained by the general geometry of the casting machine. With the twin-roll process there is the problem that the roll diameters become unpractically large for high speed casting. There is no productivity problem with the single-belt process, but there are other difficulties. Results are given on the control of thickness uniformity of the strand. If hot rolling is linked directly to the casting the rolling speed must be slower than in the conventional process. Another challenge is hot rolling down to strip of 1 mm thickness or below. Theoretical data are presented for temperature loss and for scale growth in non-conventional hot rolling. The models were used to compute the developments of temperature and of scale thickness in the integrated single-belt casting/hot rolling lines.

### Surface Science and Technology

#### The impedance analysis of reaction kinetics at the interface between molten Sn-S alloy and ZnCl<sub>2</sub>-NaCl salt

*S. WANG et al.*

The interfacial reaction between molten Sn-S alloy and ZnCl<sub>2</sub>-NaCl salt was studied by an A. C. impedance method to clarify the individual kinetic factors concerning the electrode reaction at the interface between the alloy and the salt. The total impedance between Sn-S alloy and ZnCl<sub>2</sub>-NaCl salt was measured.

The results obtained were successfully used to determine the individual kinetic factors on electrode reaction between the alloy and the salt, such as electrolyte resistance  $R_e$ , double-layer capacitance  $C_d$ , charge transfer resistance  $R_{ct}$ , rate constant of desulfurization reaction  $k_f$  and so on. When overpotential  $\eta$  equals to  $-85$  mV, these values are as follows:  $R_e = 2.93 \times 10^{-5} \Omega \text{ m}^2$ ,  $R_{ct} = 2.47 \times 10^{-5} \Omega \text{ m}^2$ ,  $C_d = 1.01 \text{ F m}^{-2}$ ,  $k_f = 2.1 \times 10^{-3} \text{ s}^{-1}$ .

### Microstructure

#### Heat treatment of weld part in 15-5 PH stainless steel and manufacturing of actual hydrofoil for a high-speed passenger craft

*A. FUJITA et al.*

Hydrofoils used for high-speed passenger crafts require characteristics such as high strength, high toughness, and high resistance to corrosion. 15-5 PH stainless steel, a precipitation hardening stainless steel, demonstrates such requirements, but welded assembly of the hydrofoil using this material basically requires re-solution treatment after welding. This causes the hydrofoil to show significant deformation, making it difficult to maintain its prop-

er configuration.

The present research work, examines heat treatment conditions intended to inhibit this deformation. The results confirmed that good mechanical properties can be provided to the welded parts and that the impact resistance of the parent material can also be greatly improved by providing solution treatment at a temperature lower than the conventional solution treatment temperature. Furthermore, a heat treatment method to inhibit deformation was elucidated by producing actual hydrofoils on the basis of these fundamental test results, and material testing of the components for the hydrofoil also confirmed that they possess satisfactory characteristics for actual use as hydrofoil material.

### Physical and Mechanical Properties

#### The formation and decomposition of Cu-C pairs in quench-aged Fe-C-Cu alloys

*K. TAGASHIRA et al.*

The formation and decomposition of Cu-C pairs in alpha-irons have been discussed in quench-aged Fe-C-Cu alloys which are five kinds of cold-drawn low carbon steel wires of 0.65 mm diameter containing copper from 0.00 to 0.55 mass%. These specimens were heated at 973 K for 600 s in argon gas, quenched into 273 K, and then isothermal-aged in an oil bath of 423 K. These were taken out from the oil bath at a suitable time during ageing for the measurement of electrical resistivity at 77 and 273 K. The difference from Matthiessen's rule (DMR) during ageing is obtained from the electrical resistivity at both measuring temperatures. The following results are obtained. (1) The electrical resistivity for all specimens decreases during ageing. However, DMR during ageing increase for the specimens except 0.00 mass% Cu specimen. The more the Cu content, the bigger the increment. (2) The behaviour above mentioned can be explained by the formation of Cu-C quasi-pairs within a very short time during quenching and by their decomposition during ageing. (3) The quasi-pairs may be formed by trapping of diffusing carbon atoms into the second nearest octahedral interstices around substitutional Cu atoms by an elastic interaction not by a chemical one. (4) The existence of Cu-C quasi-pairs are also suggested from the comparison of micro Vickers hardness of these alloys with the decarburized ones at just after quenched stage.

#### Some aspects of mechanisms and modelling of creep behaviour of 2.25Cr-1Mo steel

*S. CHAUDHURI et al.*

The present work attempts to establish experimentally the dominant mechanism based model for describing the shape of creep curve at any arbitrary stress and temperature. Creep data were collected from literature and some were generated experimentally under different microstructural conditions of 2.25Cr-1Mo steel. Influence of thermal aging and pre-strain on the shape of creep curve have also been studied.

The analysis of creep data clearly revealed that irrespective of initial microstructures, thermal aging

significantly increases the tendency to soften whereas pre-strain results in marginal strengthening. Softening due to carbide coarsening was thus established as the dominant mechanism of creep in 2.25Cr-1Mo steel.

A numerical procedure was developed to extract the parameters of the model, describing the kinetics of carbide coarsening directly from creep curves. A fairly accurate prediction of creep strain up to 5% was obtained using this approach. The kinetics of carbide coarsening was found to depend on the applied stress.

#### **Effect of Cr dopant on high-temperature embrittlement in Fe Alloys containing high concentration of Cu**

*Y.UMAKOSHI et al.*

To evaluate usage of ferrous scraps containing a high concentration of Cu, the mechanical properties of Fe-Cu alloys with 0.3~4.0 mass% Cu were examined focusing on the effect of the Cu-rich phase segregated at grain boundaries on high-temperature embrittlement; ductility improvement was attempted by adding a small amount of Cr. Excess Cu atoms in

the Fe-Cu alloys segregated and formed Cu-rich phase at the grain boundary in  $\alpha$  matrix depending on the grain boundary character. Large Cu-rich phase was susceptible to nucleation of microcracks and induced grain boundary fracture, resulting in a loss of ductility at high temperature. Addition of a small amount of Cr effectively improved ductility of  $\alpha$  Fe-Cu alloys at high temperature because the formation of Cu-rich phase was suppressed by Cr addition and/or segregated Cr increased the bonding force at grain boundaries. Ductility decreased in  $\gamma$  Fe-Cu alloys with increasing Cu concentration and this reduction was not improved by Cr addition. High strength Fe-Cu alloys containing a large quantity of Cu was obtained, however, by Cr addition.

#### **Social and Environmental Engineering**

##### **Methodology to evaluate reduction limit of carbon dioxide emission and minimum exergy consumption for ironmaking**

*T.AKIYAMA et al.*

For evaluating theoretical reduction limit of carbon dioxide emission from a conventional carbon-

based ironmaking, a new methodology of system analysis is proposed based on thermodynamics theory, together with implementation. In this method, we first define the ironmaking system by several fundamental reactions, then focus overall changes of enthalpy and exergy in the total system in order to obey first and second laws of thermodynamics, and finally derive carbon requirement and minimum exergy loss clearly. The results suggest the possibility of energy saving by indicating an ultimate goal for reducing CO<sub>2</sub> emission and difference between operating data and it. Significantly, this method is also applicable to all other metallurgical or chemical systems for studying possibility and limitation of energy saving.