

## Fundamentals of High Temperature Processes

### Determination of the rate of CO<sub>2</sub> dissociation on the surface of CaO-SiO<sub>2</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>, CaO-SiO<sub>2</sub>-CaF<sub>2</sub> and CaO-SiO<sub>2</sub>-Fe<sub>x</sub>O melts

M. MORI *et al.*

The rate constant of CO<sub>2</sub> dissociation on the surface of CaO-SiO<sub>2</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>, CaO-SiO<sub>2</sub>-CaF<sub>2</sub> and CaO-SiO<sub>2</sub>-Fe<sub>x</sub>O slags was measured by means of a <sup>13</sup>CO<sub>2</sub>-CO isotope exchange technique as functions of slag basicity, iron content, temperature and imposed equilibrium CO<sub>2</sub>/CO ratio. It was shown that CaO-SiO<sub>2</sub>-Fe<sub>x</sub>O slags with low iron content and those with high iron content had different rate determining steps. According to those rate determining steps, the apparent rate constant,  $k_a$ , was calculated for each slag. Consequently, we obtained the equations:  $k_a = k(1 - \sum_i \theta_i)$  and  $k_a = k(1 - \sum_i \theta_i)(a_{FeO_2})^2(P_{CO_2}/P_{CO})^{-1}$  for the former slag and the latter, respectively, where  $k$  is the rate constant,  $\theta_i$  is the fractional coverage of absorbed species  $i$ . From the view point of dependence of the rate constant on oxygen partial pressure, these equations well represented the experimental results. For 35 mass% CaO-65 SiO<sub>2</sub> and 50mass% CaO-50 Al<sub>2</sub>O<sub>3</sub> slags, activation energies were estimated to be 203 [kJ/mol] and 120 [kJ/mol], respectively. Addition of CaF<sub>2</sub> up to 30 mass% does not affect  $k_a$  for CaO-SiO<sub>2</sub> melts.

## Ironmaking and Reduction

### Optimization of magnetizing reduction and magnetic separation of iron ores by experimental design

M. I. NASR *et al.*

An experimental design of magnetizing reduction and magnetic separation of Egyptian low grade iron ore has been conducted using a data developed from applying the conventional single-factor experimentation in order to get the real optimum conditions of the processing. A model has been developed for magnetizing reduction to describe the relationship between the extent of reduction and the reduction temperature, time and reducing gas flow rate, whereas another model for magnetic separation process was deduced correlating the ore size and reduction time to the iron recovery in the magnetic concentrate.

### Effect of reducing gas on the volume change during reduction of iron oxide

A. A. EL-GEASSY *et al.*

Iron oxide compacts fired at 1 373 K for one hour were reduced at 973-1 373 K using different reducing gases; namely CO, H<sub>2</sub>, 50 % H<sub>2</sub>-CO and simulated reformed natural gas. The reduction course has been followed up by means of recording weight-loss changes as a function of time. The structure of the com-

pacts was examined by reflected light microscope whereas the volume change was measured by displacement method. It has been found that both temperature and reducing gas composition have a significant effect on the volume change behaviour during reduction. The volume change values of the completely reduced compacts were not well representing the volume change behaviour during reduction. The greater swelling was observed for compacts reduced with pure CO giving a maximum value of 224 % for compacts reduced up to 90 % reduction at 1 173 K. Reduction with pure H<sub>2</sub> showed a maximum contraction of 24 % for compacts completely reduced at 1 123 K. The volume change behaviour for compacts reduced with gas mixtures was mainly dependant on the relative contents of CO and H<sub>2</sub> in the reducing gas. Mechanisms have been proposed for the volume change trends for compacts reduced with the different gases and correlated with the microstructure of the reduced compacts.

### High rate coal injection of 218kg/t at Fukuyama No. 4 blast furnace

A. MAKI *et al.*

At Fukuyama No. 4 Blast Furnace, a pulverized coal injection system with a capacity of 72 t/h was installed at the end of April 1994. In October, six months later, the highest coal injection was carried out. Eventually, a maximum injection rate of 230 kg/t and monthly average of 218 kg/t was successively attained. The main features making the high rate injection of pulverized coal possible are the following:

- (1) high combustion efficiency with the newly designed eccentric double lance;
- (2) use of Hybrid Pelletized Sinter with superior reducibility and melting characteristics; and
- (3) optimum control of gas flow distribution to keep in-furnace permeability.

Moreover, the in-furnace phenomena in the lower part were analyzed by the deadman prove, and it was confirmed that the good permeability in the deadman could be maintained by the improvement of injection lance and burden properties.

## Steelmaking and Refining

### Characterization of slag-metal droplet-gas emulsion in oxygen steelmaking converters

B. DEO *et al.*

Metal droplets of various sizes are ejected from the jet impact zone in oxygen steel making converters. The residence time of these droplets in the surrounding gas-slag mixture is calculated for different operating conditions in top blown converters. A new dimensionless emulsion number,  $En$ , based on the ratio of the residence time of the metal droplets to the

residence time of gas bubbles in liquid slag is proposed. This emulsion number is found to be strongly dependent on the ratio of lance height to the throat diameter of De Laval nozzle. The blowing regimes followed in three plants are analyzed in terms of emulsion number. The reduction of FeO in slag by dissolved carbon in metal droplets also depends upon emulsion number and, in turn, decides the lance height chosen at various stages of the blow as well as lime dissolution, slag formation and slopping. The emulsion number can be used as an effective tool to control slag formation behaviour.

### Melt flow characterization in continuous casting tundishes

Y. SAHAI *et al.*

Melt flow in continuous casting tundishes is normally characterized by a combined model. The model is used to analyze the residence time distribution of fluid in a tundish. In this model, the fluid volume in tundish is considered to be consisting of the plug flow, well-mixed flow, and dead volumes. Although this model was proposed over 20 years ago, most researchers have either used it incorrectly or made an assumption in analyzing melt flow in tundishes. Both approaches may lead to incorrect and misleading calculations of the dead volume. In this paper, the combined model has been discussed and its correct application to tundish melt flow has been outlined.

## Casting and Solidification

### Thermo-fluid-dynamics modelling of the solidification process and behaviour of non-metallic inclusions in the continuous casting slabs

A. FERRETTI *et al.*

A numerical model has been fitted and used to describe the main features of the steel casting and solidification process. Information on the interaction between the thermal aspects (temperature trends at the slab surface and development of the shell growth) and the fluid-dynamics ones (flow pattern inside the mould and at the meniscus) has been achieved. In the latter case, such a tool allows checks on the operating conditions, in particular size and shape of the Submerged Entry Nozzle (SEN). In the former, it gives data on the superheat dissipation and the shell growth rate, also allowing an evaluation on the microstructure. Starting from the so obtained thermo-fluid-dynamics field, the path of typical non-metallic inclusions has finally been described, and comparison with experimental and literature data has been made as far as their impact point on the growing shell is concerned.

### A criterion for water modeling of non-isothermal melt flows in continuous casting tundishes

C. DAMLE *et al.*

Water modeling of tundish melt flows offers

useful insight into the underlying flow phenomena occurring in the tundish. To date most of the water modeling studies have been carried out under isothermal conditions; usually at room temperature. However, fluid flow in continuous casting tundishes is normally not isothermal. By analyzing the dimensionless turbulent Navier-Stokes equation, a modeling criterion is proposed which may be adequate to simulate the flow of molten metal in continuous casting tundishes by means of water modeling. The criterion was tested for a few hypothetical test cases by means of water modeling as well as mathematical modeling. Good agreement between the residence time distribution curves was obtained in the test cases considered when the proposed modeling criterion was satisfied.

#### **Relationship between flow characteristics and surface quality in inclined twin roll strip casting**

*J.D. HWANG et al.*

Good surface quality is essential for the twin roll cast stainless steel strip to be directly cold-rolled. Thus, surface quality of AISI 304 stainless steel is one of the main problems for the twin roll strip casting process to be put into commercial production. The surface defects commonly appeared in the as-cast strip of twin roll process may include longitudinal and transverse cracks or wrinkles as well as unevenness which is mainly caused by gas trapping and surface vibration of meniscus between the two rolls.

In this study, a modeling software was applied to simulate the flow behavior of molten pool at quasi-steady state in inclined twin roll strip casting and to investigate the relationship between flow characteristics and surface quality of the produced thin strip. The flow characteristics was drawn from the calculated flow patterns and then correlated to the surface quality of thin strips produced in an experimental caster under the same casting condition as the calculations. Through this procedures, several correlations were then found. First, the surface wrinkles appeared on the thin strip when the pool levels were low. The problem was improved with a higher pool level due to less flow violence nor meniscus fluctuation. Second, the recirculation with a large vortex occurring around the triple intersection point of the roll/melt/air three phases was the main cause for the slag and/or dross trapping. Third, by using a higher roll angle along with an inclined feeding position nearer to the lower roll, a much stable flow on the meniscus surface could be obtained.

#### **Analysis and Characterization**

#### **Glow discharge optical emission spectrometry on the formation of thin oxide layers on the iron binary alloy surface**

*S. SUZUKI et al.*

Glow discharge optical emission spectrometry (GDOS) has been used for characterizing thin oxide layers formed on iron-base binary alloys with aluminum, silicon, phosphorus, chromium, manganese, nickel and molybdenum by heating in air at 773 and 873 K. We focused on the enrichment of alloying elements in the thin oxide layers and substrates as well as the effect of alloying elements on the thickness of the oxide layers. It was found in the quantitative depth profiles that aluminum, silicon, phosphorus, chromium and nickel are enriched at the oxide/metal interface, while manganese is distributed to the oxide layer and molybdenum is observed neither at the oxide/metal interface nor in the oxide layer. It is also suggested that aluminum, silicon, chromium and molybdenum have a significant influence on the reduction in the thickness of the oxide layers, and the present results are in good agreement with structural data obtained by X-ray diffraction.

#### **Surface Science and Technology**

#### **Basic investigation of CVD method for manufacturing 6.5 % Si steel sheet**

*K. OKADA et al.*

It has been known for a long time that 6.5 % Si steel sheet has excellent soft magnetic properties that make it well suited for use as a magnetic material. However, steel of that composition is brittle and has little ductility; for this reason, the material could not be manufactured on an industrial scale with conventional cold rolling methods.

Here, the authors studied and devised a method for continuously producing 6.5 % Si steel sheet utilizing the CVD (Chemical Vapor Deposition) method. In this method, 6.5 % Si steel sheet is continuously produced with the following procedure: first, low-Si steel, an easy-to-roll material, is rolled beforehand to produce thin strip; then, the CVD treatment using a gas containing  $\text{SiCl}_4$  is applied to the strip so that silicon is permeated through the surface of the steel strip; and finally, the strip is given a diffusion annealing to uniformly distribute the silicon throughout. While the siliconizing of steel has previously been studied as a way to improve the corrosion resistance of steel, this work marks the first study of this method as a way to produce 6.5 % Si steel sheet on an industrial scale.

The authors examined the basic conditions required for the process—the process for manufacturing 6.5 % Si steel sheet utilizing this type of CVD-based siliconizing treatment technology—by carrying out a theoretical study of related chemical reactions and performing basic research with a simple test apparatus. Based on the results, the authors next conducted an investigation to develop a method for continuously manufacturing the steel in coil form and finally proposed an overall process

configuration to realize such a production system.

#### **Improvement in the corrosion resistance of zinc-plated steel by electrodeposition of magnesium from a molten salt**

*M. MORISHITA et al.*

Electrodeposition of magnesium on zinc-plated steel from a molten salt electrolyte was investigated in order to improve its corrosion resistance. The 55 mol% LiCl-39 mol% KCl-5 mol%  $\text{MgCl}_2$ -1 mol% CsCl molten salt was used for the electrodeposition of magnesium on zinc-plated steel. The primary crystallization temperature of the salt is 574 K, which is 119 K lower than the melting point of zinc. The molten salt gave homogeneous electrodeposition of magnesium on a zinc-plated steel at 653 K. The magnesium electrodeposited diffused into the zinc layer of the zinc-plated steel during electrolysis. In 5 mass% NaCl aqueous solution at room temperature, the magnesium-deposited zinc-plated steel did not form red rust for 41 days whereas the zinc-plated steel formed red rust after 10 days. The red rust, which was formed at 41 days on the magnesium deposited zinc-plated steel, had localized for further 21 days without expanding. This fact suggests that the magnesium-deposited zinc-plated steel have a self healing ability. Moreover, in a salt spray test at 308 K, the time of generation of red rust for the magnesium-deposited zinc-plated steel was 10 times longer than for the conventional zinc-plated steel.

#### **Microstructure**

#### **Spreadsheet modelling of grain size evolution during rod rolling**

*T.M. MACCAGNO et al.*

An analysis was conducted of the pass-by-pass evolution of austenite grain size during the rod rolling of plain carbon steel. This was achieved by organizing previously-developed equations relating grain size and hot working parameters into commercial computer spreadsheet program. By considering the substantial "redundant" strains developed during rod rolling, the analysis reveals that metadynamic recrystallization (MRX) is the dominant microstructural process, and this is confirmed by the mill grain size measurements reported previously. The spreadsheet was also employed to examine the effects of modifications to rod rolling practice aimed at refining the austenite grain size. Little benefit is obtained by increasing the strain rate or by reducing the distance from the final rolling pass to the laying head. On the other hand, increasing the cooling rate on the forced-air cooling deck should lead to measurable grain refinement. Lowering the temperature during rolling can lead to even more refinement, and various strategies to achieve this are discussed.

### Characteristics of static and metadynamic recrystallization and strain accumulation in hot-deformed austenite as revealed by the stress relaxation method

*P. KARJALAINEN et al.*

The newly established technique of stress relaxation has been applied to measure the kinetics of static and metadynamic recrystallization of austenite in a low-carbon steel subsequent to compression executed at a strain rate of 0.1 or 0.01 s<sup>-1</sup> at 900°C or 1000°C. The characteristics of static recrystallization were found to be consistent with those previously reported from double-stage deformation tests. Metadynamic recrystallization, contrary to static one, showed no dependence on strain and hardly any on temperature, but significant dependence on strain rate. The Avrami exponents were almost identical for the two processes, about 1.5-1.6 at 0.1 s<sup>-1</sup>, but decreased to 1.0-1.3 at 0.01 s<sup>-1</sup>. Metadynamic recrystallization resulted in complete softening except when relaxed after compression to a strain of 0.3 or beyond at a low strain rate of 0.01 s<sup>-1</sup>. The law of mixtures approach was found to be more accurate than the uniform softening model to describe recrystallization in partially recrystallised and subsequently deformed aus-

tenite. The results confirm the feasibility of the stress relaxation technique as an efficient method for investigating recrystallization kinetics in hot-deformed austenite.

### Physical and Mechanical Properties

#### A prospect of grain boundary engineering for electronic properties in polycrystalline materials (Review)

*L. FIONOVA et al.*

Recent studies of electronic properties of individual grain boundaries (GBs) have been reviewed in relation to the character and structure of GBs in metals, semiconductors and superconducting materials. The effects of grain assemblage and cooperative phenomena in GB ensemble on electrical and magnetic properties have been also discussed. Using these results as a base, possible ways for GB design and control and prospective of GB engineering are given.

#### Effect of nitrogen on the high temperature creep behavior of 9Cr-2Co steel

*K. HARA et al.*

Constant load creep tests were conducted at 873, 898 and 923 K under an initial stress of 50, 60 or 70 MPa to examine the effect of nitrogen addition (0.06, 0.11, 0.16 and 0.19 wt.%) on a 9wt.% Cr-2wt.% Co ferritic steel. Extraction residue analysis showed that about 60 to 80 % of added nitrogen was present as a supersaturated solid solution. The rest of the nitrogen formed nitride precipitates. The minimum creep rate decreased and creep rupture life increased with the increase of nitrogen content. It is also observed that the higher the nitrogen content, the shorter the creep rupture strain. Creep state equation could be represented as follows;  $\dot{\epsilon}_0 = A_0 \sigma_0^n \exp(-Q_0/RT)$ , where  $\dot{\epsilon}_0$  is the imaginary initial strain rate defined in the text,  $A_0$  is a constant,  $n$  is the stress exponent and  $Q_0$  is the apparent activation energy. Mean values of  $n$  and  $Q_0$  were 4.5 and 360 kJ/mol, respectively. The magnitude of stress exponents and the dependence of  $\dot{\epsilon}_0$  upon soluble nitrogen concentration suggest that the rate controlling mechanism is the glide motion of dislocations dragging I-S atmospheres. It is also found that the Orowan stress increased with the increase of total nitrogen concentration.