

## Fundamentals of High Temperature Processes

### Bubble behaviour and absorption rate in gas injection through rotary lances

M.C.DIAZ *et al.*

Bubble behaviour and absorption rate of gas injected into a liquid bath through rotary L-shaped lances were studied by cold models. A high-speed video recording system was used to measure the bubble diameter and the rising velocity. The absorption rate of injected CO<sub>2</sub> gas in aqueous NaOH solution was measured by using a pH meter.

It is found that the lance rotation leads to a decrease in the bubble diameter and the rising velocity as compared with the stationary lance. The bubbles produced by a multi-hole lance are smaller than those produced by a single-hole lance. The reduction in the bubble rising velocity is connected with the decrease in the bubble diameter, distribution of bubbles over the liquid bath and distortion of the bubble rising path due to the lance rotation.

The gas absorption rate for the rotary lances is larger than that for the stationary lance. The effect of the rotation speed on volumetric mass transfer coefficient is larger at lower gas flow rate. The multi-hole lance can increase the volumetric mass transfer coefficient by about three times larger than the single-hole lance.

The results are discussed in terms of the bubble coalescence, mass transfer coefficient and total interfacial area between bubbles and liquid.

### Cold model experiments of gas removal from molten metal by an irradiation of ultrasonic waves

M.KOBAYASHI *et al.*

Application of the technique of removing dissolved gas by irradiating of ultrasonic waves on a molten metal system was discussed. In water model experiments, dissolved gas can be removed by "rectified diffusion" and the apparent removal rate constant increases linearly with the input power. The addition of non-wettable particles to the bath enhances the degassing. A mathematical model of rectified diffusion suggests that it would be difficult to apply the technique to the gas removal in practical steelmaking processes, where the gas concentration must be controlled to a ppm level. However, since Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are non-wettable to molten iron, it is promising that small inclusions can be removed by the bubbles generated by ultrasonic waves in a molten iron system.

## Ironmaking and Reduction

### Synthesis of iron carbide by reaction of iron ores with H<sub>2</sub>-CO gas mixtures bearing traces of sulfur

S.HAYASHI *et al.*

Particles of hematite ores in a porcelain boat were reduced and carburized at 823-1223K by H<sub>2</sub>-CO mixtures under low sulfur pressures where metallic iron remained stable. Within major of these various conditions nearly one hour reaction could convert their particles completely to iron carbides such as mostly Fe<sub>3</sub>C. It was found that traces of gaseous sulfur makes iron carbides enough stable rather than free carbon or metallic iron. Their conversion yields were insensitive to inlet H<sub>2</sub>/CO mole ratio and ore type. Total sulfur contents in products obtained for lower sulfur pressures were as low as conventional reduced irons.

## Steelmaking and Refining

### A kinetic model applied to the molten pig iron desulfurization by injection of lime-based powders

V.SESHADRI *et al.*

A kinetic model of hot-metal desulfurization by deep injection of synthetic powder mixtures is presented. The approach takes into consideration the transient contribution due to the particles dispersed in the bulk metal and those located at the bubble-metal interface, the influence of the carry-over slag as well as the volume and composition of the top slag. The model has been utilized to assess the influence of the treatment temperature, rate of injection of powder mixtures, gas flowrate and initial concentration of sulphur over the desulfurization kinetics. In the second part of this study an analysis of the industrial data for injection of powder mixtures using this model is described.

### Decarburization of iron melt by an immersed Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> porous tube

M.AHMADI NAJAFABADI *et al.*

A porous Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> tube, the inside of which is evacuated, is used to decarburize molten iron. Effects of inside pressure and Fe<sub>2</sub>O<sub>3</sub> content of the porous tube, initial carbon content of the melt and melt temperature on the decarburization rate are investigated. Evacuating the inside of the tube reduces the partial pressure of CO at the tube-melt interface and enhances the decarburization reaction. However, in the case of lower initial carbon content of the melt, liquid slag is formed at the surface of higher Fe<sub>2</sub>O<sub>3</sub> content tube, and sucked into its pore. Penetration of the liquid slag into the tube reduces the thermal strength and leads to the tube deformation. As a result, the gas permeability of the tube is decreased, and the decarburization rate becomes lower. The apparent decarburization rate constant (apparent first-order rate con-

stant) for the non-deformed tube increases with increasing Fe<sub>2</sub>O<sub>3</sub> content and decreasing inside pressure of the tube. At higher carbon contents, the tube is not severely deformed, but the effect of evacuation on the decarburization rate is little due to formation of large amount of CO (or CO boiling). The apparent decarburization rate constant decreases with increasing initial carbon content, and hence the rate is presumed to be controlled mainly by oxygen supply from the tube. The apparent activation energy for the decarburization reaction is 72.5 kcal/mol.

## Casting and Solidification

### Stochastic modeling of solidification grain structures of Al-Cu crystalline ribbons in planar flow casting

K.-Y.LEE *et al.*

A stochastic model has been developed for the prediction of polycrystalline microstructure formation in planar flow casting. The present model was based on the coupling of the finite volume (FV) method for macroscopic heat flow calculation and a two-dimensional cellular automaton (CA) model for treating microstructural evolution in planar flow casting. The CA model takes into account nucleation and growth kinetics. Heterogeneous nucleation can occur on nucleation sites both at the wheel surface and in the bulk liquid with random crystallographic orientations. The growth kinetics of a dendrite tip was evaluated using the Lipton-Kurz-Trivedi(LKT) model by which the relationship between the growth velocity of a dendrite tip and the local undercooling was calculated. At each time interval, the latent heat released by the growing cells in the CA model was fed back into the control volume containing those cells in order to calculate the temperature distribution for the following step of calculation. The present model has been applied to predict the cooling curves and the resultant microstructures of Al-Cu polycrystalline ribbons spun by planar flow casting. The effects of wheel speed, alloy composition, and superheat of the melt on grain structures were investigated. Variation in interface velocity of the growing cell with distance from the wheel surface was also analyzed in order to investigate microstructural transition in ribbons. The calculated grain structures were in good agreement with those obtained experimentally.

## Analysis and Characterization

### Development of an automatic analyzer for a mixed nitric acid, hydrofluoric acid, and iron ion in the pickling process

M.ITO *et al.*

The method of sulfuric acid analysis is well established. At present, the concentration of sulfuric acid can be analyzed automatically on

actual production lines by using neutralization titration method. With the case of a mixed solution of nitric and hydrofluoric acid, however, measuring each acid content and the concentration of iron contained therein with speed and accuracy suitable for actual operation is very difficult even using the presently available acid separation techniques. A primary reason for this is that no piece of equipment with that level of measuring capability has not been developed yet.

In the preliminary studies, the following are verified:

(1) As a method of analyzing hydrofluoric acid, the iron-acetylaceton complex discoloration absorbance method is adopted.

(2) As a method of analyzing nitric acid, the method of subtracting the concentration of hydrofluoric acid from the total acid amounts obtained by neutralization titration is adopted.

(3) As a method of analyzing the iron content, the iron-salicylic acid complex absorbance method is adopted.

By fully automating the series of analytical processes described above, the following are achieved:

(1) The several hours needed to complete the analysis work can be shortened to about 40 min. Moreover, acid can be controlled with care and attention to detail, which will greatly contribute to the improvement of the quality of pickled coils.

(2) The work load of line operators can be reduced, making substantial labor saving possible.

## Surface Science and Technology

### Inhibition of anodic dissolution of zinc-plated steel by electrodeposition of magnesium from a molten salt

*M. MORISHITA et al.*

Inhibition of anodic dissolution of zinc-plated steel by electrodeposition of magnesium from the 55mol%LiCl-34mol%KCl-55mol%MgCl<sub>2</sub>-1mol%CsCl-5mol%KI molten salt was investigated. On a heat-treatment, the zinc layer changed to 3 layers: the outer layer; the inner layer; interface layer just on the substrate steel. Four steps of anodic dissolution were observed in the anodic polarization curves in 5mass%NaCl aqueous solution. The first step was the anodic dissolution of the MgZn<sub>2</sub> and Mg<sub>2</sub>Zn<sub>11</sub> in the outer layer and the inner layer. The second one was the active dissolution of the remaining zinc in the inner layer. The third one was the active dissolution of the  $\Gamma_1$  phase in the interface layer. The fourth step was the active dissolution of the matrix steel. It should be noted that the anodic current density of the first step was very small in comparison with the others. The present results suggested that the intermetallic compounds, MgZn<sub>2</sub> and Mg<sub>2</sub>Zn<sub>11</sub>, make a protective films on the surface, inhibit the anodic dissolution and give the high corrosion resistance to

the magnesium-deposited zinc-plated steel.

## Microstructure

### Effect of boron addition on microstructure and properties of sintered Fe-1.5Mo powder materials

*E. DUDROVÁ et al.*

The microstructure formation and mechanical properties of sintered materials based on the prealloyed Fe-1.5wt%Mo powder with 0.2-0.6wt% of boron addition are investigated. An eutectic liquid phase Fe+Fe<sub>2</sub>B activating the sintering of Fe-1.5Mo+B powder systems is formed. Besides this, an interaction of boron with the Fe-Mo prealloyed matrix occurred and the formation of fine precipitates containing molybdenum and boron was registered. Due to this interaction the decrease of eutectic phase portion and strengthening of the matrix by borides occurred. The materials Fe-1.5Mo+0.4wt%B achieved the tensile strength R<sub>m</sub>=487 MPa, the elongation A<sub>5</sub>=2.5% and the hardness of 212 HV 30 at the density of 7.15g.cm<sup>-3</sup> after sintering at 1200°C for 30 min.

### Magnetic analysis of precipitation and coarsening of carbides in steels

*H. HILDEBRAND*

Dispersion microstructures in C, Cr- and Mn-alloyed steels result from the precipitation and coarsening of carbide particles from the martensitic initial condition. The changes in the microstructure were observed at aging temperatures T=500, 600, 650 and 700°C and for the time t=1 to 4 290 min. by measuring the coercive field strength H<sub>c</sub>. The particle size analysis on scanning electron micrographs of M<sub>3</sub>C in the steels and of M<sub>6</sub>C (+MC) carbide particles in the case of the high-alloyed steel X80WMo6.5 yielded to a certain connection with H<sub>c</sub>. Thus H<sub>c</sub> can be taken as an indirect microstructural characteristic quantity instead of directly observed microstructure data.

It was found that nucleation, growth and the dominating coarsening of the particles take place permanently in so-called generations. With increasing time the particle sizes in the one after another following generations become smaller because of the matrix depletion of the participated elements by precipitation. The Ostwald-ripening law is to apply separately to each generation. All the processes and relationships, which are connected with H<sub>c</sub>, can be written mathematically.

### Effect of manganese on aging in low carbon sheet steels

*S. K. CHANG et al.*

For the investigation of the effect of manganese of aging in the low carbon steels the manganese content was varied from 0.02 to 0.25 wt.% in the 0.02 wt.% C steel. The low manganese containing steel reveals lower aging index than the high manganese steel. The aging

index decreases with a decrease of manganese content and an increase of coiling temperature, because (1) the amount of solute manganese playing a role in obstructing the movement of solute carbon into the interface of carbide-ferrite, resulting in the hinderence of the carbide growth, is not sufficient and (2) the coarse carbide formed in the hot band with higher coiling temperature is crushed into small fragments during cold rolling, resulting in the development of numerous micro-voids at the fragments, which provide the numerous sites for the precipitation of solute carbon.

### Epsilon and eta phases precipitated in an Fe-38 Ni-13Co-4.7Nb-1.5Ti-0.4Si superalloy

*K. KUSABIRAKI et al.*

An Fe-38Ni-13Co-4.7Nb-1.5Ti-0.5Si alloy is a controlled low thermal expansion superalloy with a good resistance to SAGBO (Stress Accelerated Grain Boundary Oxidation) embrittlement at elevated temperatures by an intentional Si addition. The precipitation of second phases,  $\epsilon$  phase,  $\eta$  phase and so on, in this superalloy is investigated by means of optical microscopy, scanning electron microscopy, transmission electron microscopy, and X-ray diffractometry. A time-temperature-transformation diagram for the  $\epsilon$  phase is presented. The crystal structure and the lattice parameters of the  $\epsilon$  phase and the orientation relationship with the alloy matrix  $\gamma$  are determined. It is shown that the  $\epsilon$  phase is not a stable phase as well as  $\gamma'$  phase, but cellular  $\eta$  phase is the most stable precipitation phase in this alloy.

## New Materials and New Processes

### Grain refinement of combustion-synthesized NiAl by addition of Al<sub>2</sub>O<sub>3</sub> particles

*K. MATSUURA et al.*

An intermetallic compound of mononickel aluminide (NiAl) is combustion-synthesized from a mixture of nickel and aluminum powders by a pseudo-Hot-Isostatic-Pressing (pseudo-HIPing) method. The effects of the addition of alumina (Al<sub>2</sub>O<sub>3</sub>) particles on the microstructure and mechanical properties of the combustion-synthesized NiAl is investigated. The density and hardness of the NiAl significantly increase with increasing pseudo-HIPing pressure applied during the combustion synthesis. The increase in the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> particles leads to a slight decrease in the density of the NiAl, but it does not affect the hardness. The grain size of NiAl decreases, as the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> particles increases and as the size of the Al<sub>2</sub>O<sub>3</sub> particles decreases.