

**Fundamentals of High Temperature Processes****Evaporation of copper from iron melts**A.I.ZAITSEV *et al.*

The Knudsen-cell mass spectrometry and the integral Knudsen effusion technique under ultra-high neutral vacuum were used to study evaporation of pure Fe, Cu and molten Fe-Cu alloys containing up to 10.1 mol% Cu in the temperature range of 1440 to 1916 K. Standard sublimation enthalpies of Fe and Cu and thermodynamic characteristics of the Fe-Cu liquid solution were calculated. The obtained results and literature data were applied for assessment of potentialities of steel decopperizing technology based on evaporation. The time required for a decrease in Cu concentration from 0.6 to 0.3 wt% through evaporation from the exposed surface of a 160-tons ladle into vacuum of 100 Pa amounts to 5 h. Decopperizing can be accelerated by combination of vacuum treatment with blowing neutral gases through the molten metal. Two processes are responsible for removal of copper in this case: transfer into gas bubbles, free-rising from the ladle bottom to its surface, and evaporation from molten metal surface, turbulized by blowing-through gas. The length of treatment required for the above decrease in copper concentration under the most favorable conditions (the highest vacuum over the ladle and the highest velocity of gas-stream blowing through the molten metal used in metallurgy) reduces to 1.5 h.

(cf. *ISIJ Int.*, 44 (2004), 639)**Theoretical study on separation of nonmetallic inclusion particles from a hollow cylindrical melt in alternating electromagnetic field**K.Li *et al.*

Kinetic analysis was made on the electromagnetic separation of nonmetallic inclusions from hollow cylindrical melt in an alternating electromagnetic field. Effects of various processing parameters such as magnetic flux density  $B_c$ , imposing time  $t$ , particle diameter  $d_p$ , the nondimensional parameters  $r_1/\delta$  and  $\lambda$  on the removal efficiency  $\eta$  were analyzed theoretically. It is found that higher removal efficiency can be obtained in the hollow cylindrical melt than in the solid cylinder case under the same conditions. Generally, in order to obtain higher removal efficiency, the value of various parameters should be selected properly in hollow cylindrical melt case. For the inclusion particles with diameter larger than 5  $\mu\text{m}$ , the removal efficiency can exceed 90 pct in the hollow cylindrical case with optimal processing parameters.

(cf. *ISIJ Int.*, 44 (2004), 647)**Investigation of the wetting characteristics of liquid iron on mullite by sessile drop technique**E.KAPILASHRAMI *et al.*

In the present work, reactions occurring between molten iron containing varying amounts of oxygen and mullite substrate were investigated through optical sessile drop experiments. The reactions were followed in static as well as dynamic modes through contact angle measurements. Further, the reactions

were followed as functions of time, temperature and oxygen partial pressure. The latter was changed by means of imposing a gas mixture of Ar-CO-CO<sub>2</sub> into the furnace.

The results showed that the contact angle between the substrate and the iron in purified argon gas was lower than the contact angles reported in literature for alumina and silica. Formation of a ternary slag during the reaction was observed and was subjected to SEM and EDS analysis. The thermodynamic criteria for slag formation and possible mechanisms of the reaction are discussed in the light of the experiments.

The results are of relevance in understanding the mechanism of corrosion of aluminosilicate refractories by molten iron.

(cf. *ISIJ Int.*, 44 (2004), 653)**Molecular dynamics analysis of the effect of F on the structure of molten Na<sub>2</sub>O-NaF-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system**Y.SASAKI *et al.*

For the molten quaternary Na<sub>2</sub>O-NaF-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system at 1673 K, the effect of F ion on the distribution of Si and Al tetrahedral complex anions, and the relationship between the Si and Al tetrahedra has been investigated by applying molecular dynamics simulation. In the calculation, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents in the melts were all fixed to 50.0 and 16.6 mol% respectively and only the ratio of Na<sub>2</sub>O/Na<sub>2</sub>F<sub>2</sub> was changed. It was found that NaF in the aluminosilicate melts was able to work as a network modifier for Al tetrahedra linkages but not for Si ones. Namely, F can break the linkage between Al tetrahedra and coordinate to Al tetrahedra. The replacement of nonbridging oxygen in Si tetrahedra by F ions was possible since the calculated results showed the existence of a small amount of F coordinated to Si tetrahedra.

(cf. *ISIJ Int.*, 44 (2004), 660)**Recovery rate of chromium from stainless slag by iron melts**T.NAKASUGA *et al.*

The kinetic behavior of Cr<sub>2</sub>O<sub>3</sub> reduction by iron melts containing carbon, aluminum and silicon were investigated at various conditions in order to understand effective slag treatment for recovery of chromium from stainless slag. It was found that the recovery rate of chromium was fairly slow, but it was considerably accelerated by the addition of some fluxes, such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> to the slag, which promoted the formation of liquid slag at the early stage of the reaction, and the recovery ratio of chromium was also improved. In addition, SiO<sub>2</sub> addition was more effective for increasing the chromium recovery than Al<sub>2</sub>O<sub>3</sub> addition due to the effect of CaO/SiO<sub>2</sub> ratio of slag on the reduction rate of Cr<sub>2</sub>O<sub>3</sub> in slag. The experimental results were well simulated by the previous kinetic reaction model based on two-film theory. The modeling study showed that the transfer rate of chromium from slag to metal was controlled by the mass transport in the slag phase.

(cf. *ISIJ Int.*, 44 (2004), 665)**Ironmaking****Rate of direct reactions measured in vacuum of iron ore-carbon composite pellets heated at high temperatures: influence of carbonaceous materials, oxidation degree of iron oxides and temperature**Y.IGUCHI *et al.*

The nine kinds of the composite pellets of 3.5 to 5.5 mm in diameter composed of the mixtures of wustite, magnetite or hematite and coal char, coke or graphite, in which the mol of the reducible oxygen was made equal to the mol of the fixed carbon, was heated in vacuum. The weight loss during heated at 1000 to 1200°C was gravimetrically measured. The influence of the diameter was negligible within 5.0 mm. The temperature dependence of the rate of the direct reactions of all the composite pellets was very strong. At 1000°C, the rate was such slow that it requires more than 2 ks to reach  $F_1=0.2$  and, at 1200°C, the rate was so fast that it is completed in a few hundreds seconds. The direct reactions of the char or coke bearing composite pellets proceed in two steps; the first step is very fast and temperature-independent, and the second step is the temperature-dependent process. On the contrary, the direct reactions of the graphite bearing composite pellets proceeds in three steps at 1100 and 1150°C; the first step is also very fast and temperature independent, and the much slower second step follows until metallic iron is formed. Just after the metallic iron starts to form, the reactions are accelerated as the third step. This third step of the graphite composite pellets is much faster than the second step of the char or coke bearing composite pellets. The maximum pressure inside the pellets simulated by the uniform reaction model indicates the negligible effect of the indirect reactions.

(cf. *ISIJ Int.*, 44 (2004), 673)**Casting and Solidification****Interaction between argon gas bubbles and solidified shell**H.ESAKA *et al.*

In order to investigate the interaction between gas bubbles and solidified shell, *in-situ* observations using transparent substance have been made. The movement of argon gas bubbles has been observed and recorded by a VTR. The effect of diameter of gas bubbles, the angle of a copper plate and solid/liquid interfacial morphology on the entrapment of gas bubbles have been characterized. The entrapment of bubbles increases with decreasing the diameter of gas bubbles and with increasing the angle of the copper plate. Furthermore, it is found that the entrapment of gas bubbles increases with increasing the roughness of the solid/liquid interface. A physical model has been developed taking the force balance affecting a bubble into account. Using this model, the results of the present experiment have been consistently interpreted.

(cf. *ISIJ Int.*, 44 (2004), 682)

## Effect of crystallinity on thermal diffusivities of mould fluxes for the continuous casting of steels

M.HAYASHI *et al.*

The thermal diffusivities of mould flux having the glassy and crystalline states were measured as a function of temperature by the laser flash method to obtain the relationship between the thermal diffusivity and the degree of crystallization. The thermal diffusivities of the liquid mould flux were also measured to compare the data with those of the solid samples. The thermal diffusivity increases roughly linearly with an increase in the degree of crystallization. The thermal diffusivities of glassy and liquid samples having the ratios of  $NBO/T=1.48, 1.65$  and  $2.11$  exhibit roughly the same values of  $4.6 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  and  $4.0 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ , respectively. It is considered that because the silicate network is largely broken down, there is not a significant change of the structure for these samples.

(cf. *ISIJ Int.*, **44** (2004), 691)

## Chemical and Physical Analysis

### Simple, rapid and sensitive determination of bismuth in iron and steel based on in-line preconcentration/separation directly coupled with spectrophotometric detection in a continuous flow system

T.YAMANE *et al.*

A novel flow injection system is presented for simple, rapid and selective determination of bismuth at sub-ppm levels in iron and steel by coupling in-line anion exchange preconcentration/separation directly with spectrophotometric detection. Bismuth in 0.5 M HCl solution was adsorbed on a small column packed with Dowex 1X8 anion exchange resin and desorbed with a small volume of 0.5 M  $\text{H}_2\text{SO}_4$ , which allowed effective preconcentration/separation of bismuth from a large excess of iron(III) and other coexistent elements in the steel samples. Bismuth was detected by complex formation with iodide in 0.5 M  $\text{H}_2\text{SO}_4$  yielding a yellow color. Various analytical parameters were investigated, and optimal conditions and manifold configurations were established. A linear calibration using a 10 m sample loop was obtained for bismuth in the range of 0.005–0.30 ppm. The relative standard deviation for 0.1 ppm bismuth in the solution was 0.8% ( $n=5$ ). The estimated limit of determination is ca. 0.2 ppm in steel sample when a 5 m sample loop (1.0 mm i.d.) is used. The results for analyses of steel samples by the present FI system correspond well with those obtained by AAS methods. The present FI system affords a rapid and simple analysis: only 12 min is required for analytical measurement after sample injection, and no complicated manual operation is involved.

(cf. *ISIJ Int.*, **44** (2004), 698)

## Forming Processing and Thermomechanical Treatment

### The effect of nozzle height on cooling heat transfer from a hot steel plate by an impinging liquid jet

P.LEE *et al.*

The effect of nozzle height on heat transfer of a

hot steel plate cooled by an impinging liquid jet is not well understood. Previous studies have been based on the dimensionless parameter  $z/d$ . To test the validity of this dimensionless parameter, and to investigate gravitational effects on the jet, velocity measurements were made in a liquid jet with a stagnation point, and heat transfer from a hot steel plate was investigated. Also, the critical instability point of a laminar liquid jet was examined over a range of flow rates.

The experimental velocity data for the liquid jet were well correlated with the dimensionless number  $1/Fr_z^2$  based on height. It was thought that the  $z/d$  parameter was not valid for heat transfer to an impinging liquid jet under gravitational forces; unsteady cooling experiments showed that the heat transfer was independent of  $z$  when  $1/Fr_z^2 < 0.187$ . A finite enhancement of heat transfer was observed when  $1/Fr_z^2 = 0.523$ . The discrepancy between these results and previous research is likely due to the instability of laminar liquid jets.

(cf. *ISIJ Int.*, **44** (2004), 704)

### The effect of delay time after hot rolling on the grain size of ferrite

Q.YU *et al.*

It is necessary that the yield ratio (YR) of fire-resistant steel for construction is below 0.8. However, during the industrial production of fire-resistant steel, the rapid cooling rate of the laminar cooling configuration makes the ferrite grain become fine and increases the yield ratio ( $YR > 0.8$ ). In order to reduce the YR, by using Gleeble 1500 thermomechanical simulator the experiment of the effect of delay time after hot deformation on the grain size of ferrite was carried out. The results indicate that the hot deformation can increase the system free energy and the “ledges” generate at the grain boundary of deformed austenite, which leads to the increase of the ferrite nucleation rate and the refinement of ferrite grain. However, with the increase of delayed time, that the release of deformation energy and the reduction of “ledges” would decrease ferrite nucleation rate and increase the grain size of ferrite. Based on the experimental results, the technology to prolong the delay time after hot rolling is adopted in the industry production. The tested results indicate that the technology is effective to reduce the YR of fire-resistant steel and the YR decreases to 0.79 from initial 0.84.

(cf. *ISIJ Int.*, **44** (2004), 710)

## Transformations and Microstructures

### Effect of alloying elements on the microstructure and texture of warm rolled steels

I.B.TIMOKHINA *et al.*

The effect of Cr, B and P addition on microstructure and texture formation was studied in warm rolled at 640 and 710°C interstitial free (IF) and low carbon (LC) steels. Samples were characterised using Electron Back Scattering Diffraction analysis, optical and electron microscopy.

The LC steel showed a decrease in the number of grains with shear bands compared with IF steel that

deteriorated the deformation texture. The addition of chromium to the LC steel reversed this tendency. The increase in shear band frequency in the LC(Cr) steel appears to be due to the formation of coarse  $\text{Cr}_{23}\text{C}_6$  carbides and fine strain-induced  $\text{Cr}_{23}\text{C}_6$  and  $\text{Cr}_3\text{C}_2$  carbides. Chromium addition also led to an increase in grain thickness and thus in the tendency to form shear bands. The addition of phosphorus to the LC(Cr) steel did not improve the deformation texture significantly. The addition of boron to the LC(Cr) steel decreased the number of  $\gamma$ -fibre grains and is therefore expected to reduce the formability after annealing.

Short, long, intense short and intense long shear bands were observed. Their formation depended on grain size, as well as on the amount of work hardening and precipitation hardening. The long and short (but not the intense) shear bands were linked to the presence of the  $\gamma$ -fibre after rolling.

The main outcome of this work is that the addition of alloying elements affects the volume fraction of grains containing shear bands, the grain thickness and the shear band morphology; these, in turn, affect the texture of the steel, particularly after annealing.

(cf. *ISIJ Int.*, **44** (2004), 717)

### Apparent morphologies of coarse plate martensite

Y.J.LIU *et al.*

The apparent morphologies of coarse martensite plates were researched in detail in this paper. It was found that coarse plate martensite may appear as parallel to each other, or packet, or 60° angular, or equilateral triangular, or equilateral hexagonal morphologies. Moreover, traditional ideal believing the orientation of martensite to be a chaotic and random distribution was analyzed, and showing that any martensite will combine regularly together along the habit plane pursuant to a definite pattern, hence the regular distribution of martensitic plates in space should be a spontaneous tendency. Other viewpoints concerning plate martensite were also discussed.

(cf. *ISIJ Int.*, **44** (2004), 725)

### Impact properties of thin wall ductile iron

M.CALDERA *et al.*

This work studies the impact strength of thin wall ductile iron. The properties of thin wall plates cast on sand moulds of thickness ranging from 2 to 4 mm, in which nodule counts ranging from 1 700 to 1 300 nod/mm<sup>2</sup> are measured and compared to properties obtained on samples taken from 13 and 25 mm Y blocks (ASTM A395), in which regular nodule counts are about 200 nod/mm<sup>2</sup>. Since standard Charpy specimens could not be machined from the thin plates, some complementary studies were necessary. Impact testing of ductile iron samples of regular nodule count and different widths, showed that the resilience increases noticeably and the ductile–brittle transition temperature drops as the width diminishes. The increase in the nodule count causes a significant decrease in upper shelf resilience, and a decrease in the ductile–brittle transition temperature. Very high nodule count ferritic ductile iron, of nodule count between 1 300 and 1 700 nod/mm<sup>2</sup>,

shows a ductile–brittle transition temperature of approximately  $-80^{\circ}\text{C}$  and upper shelf resilience of about  $16\text{ J/cm}^2$ . A ductile iron of similar chemical composition, but of regular nodule count, shows a transition temperature of approximately  $-26^{\circ}\text{C}$  and upper shelf resilience of approximately  $18\text{ J/cm}^2$ .

(cf. *ISIJ Int.*, **44** (2004), 731)

### Mechanical Properties

#### Effects of tramp elements on formability of low-carbon TRIP-aided multiphase cold-rolled steel sheets

*C.G.LEE et al.*

Four kinds of TRIP-aided cold-rolled steel sheets were fabricated with additions of tramp elements of Cu, Cr, and Ni to a basic 0.15C–1.5Mn–1.5Si–0.5Cu (hereafter all in wt%) steel, and their microstructures, mechanical properties, and formability were investigated to analyze the effects of the addition of tramp elements. These steel sheets were intercritically annealed at  $780\text{--}790^{\circ}\text{C}$ , and isothermally treated at  $430^{\circ}\text{C}$ . Tensile tests and limiting dome height (LDH) tests were conducted, and the changes of retained austenite volume fractions as a function of tensile strain were measured using X-ray diffraction. The formability of the Cu- and Ni-containing cold-rolled steel sheets was greatly improved as the strain-induced transformation of retained austenite was sustained up to the high strain region due to their high volume fraction and stability of retained austenite. On the other hand, the Cr-containing steel sheets showed a dual-phase structure of ferrite and martensite resulting from low volume fraction and stability of retained austenite and a large amount of transformed martensite. These findings indicated that when tramp elements such as Cu, Cr, and Ni were positively used, low-carbon TRIP-aided cold-rolled steel sheets having mechanical properties suitable for various application purposes and excellent formability could be successfully achieved.

(cf. *ISIJ Int.*, **44** (2004), 737)

### Physical Properties

#### Kinetics of metadynamic recrystallization in microalloyed hypereutectoid steels

*A.M.ELWAZRI et al.*

The isothermal kinetics of the recrystallization processes of vanadium microalloyed high carbon steels has been measured and modelled. The overall

softening data were obtained by double hit compression tests performed at temperatures between  $900$  to  $1050^{\circ}\text{C}$ , strain rates of  $0.01$  to  $1\text{ s}^{-1}$ , and inter-pass times of  $0.1$  to  $30\text{ s}$ . The recrystallization behavior above and below and the critical strain for dynamic recrystallization was investigated. The results show that there is a transition strain region between where both static and metadynamic recrystallization take place during the inter-pass time. The results also revealed that V and Si have a strong solute drag effect, on the kinetics of metadynamic recrystallization. A kinetic model is proposed which takes the V and Si concentrations into account.

(cf. *ISIJ Int.*, **44** (2004), 744)

### Social and Environmental Engineering

#### Dissolution behavior of nutrition elements from steelmaking slag into seawater

*T.FUTATSUKA et al.*

Suppression of  $\text{CO}_2$  and waste such as slags discharged from iron- and steelmaking processes are some of the typical biggest issues for the protection of global environment and sustainable growth of steelmaking industry. Utilization of active phytoplankton growth will be one of the best options to stabilize and suppress carbon dioxide at high-efficiency.

Inorganic minerals such as C, O, N, Si, P and Fe are necessary for phytoplankton multiplication. It is crucial for supply of nutrition into seawater effectively for phytoplankton multiplication to understand the dissolution behavior of some elements from steelmaking slags into seawater. Firstly, the morphology of the precipitated phases in steelmaking slags during cooling period was investigated in the present work. Secondly, the dissolution behavior of some elements from steelmaking slags and pure substances such as  $4\text{CaO}\cdot\text{P}_2\text{O}_5$  (8.5 mass% P),  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  (10.0 mass% P) and  $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$  (2.8 mass% P) solid solution phase into artificial seawater has also been studied. Thirdly, the dissolution mechanism of elements from steelmaking slags was discussed by using stability diagrams of Si, P and Fe in seawater.

(cf. *ISIJ Int.*, **44** (2004), 753)

#### Dissolution behavior of environmentally regulated elements from steelmaking slag into seawater

*T.MIKI et al.*

Steelmaking slag contains nutrition such as Si, P

and Fe for acceleration of phytoplankton growth. Phytoplankton can fixate carbon dioxide more than any other creatures on the earth. Hence, suppression of  $\text{CO}_2$  can be achieved by educating the potential of steelmaking slag as the nutrition for their propagation.

When it is considered to supply nutrition from steelmaking slag to seawater, we must avoid hazardous elements dissolution from steelmaking slag into seawater. In the present work, the dissolution behavior of Ca, Mg, Mn and F from steelmaking slags into artificial seawater was studied continuously with our previous paper. The dissolution mechanism of elements from steelmaking slags was discussed again by using stability diagram in seawater.

(cf. *ISIJ Int.*, **44** (2004), 762)

#### Recycling of sludge and dust to the BOF converter by cold bonded pelletizing

*F.SU et al.*

With the aim to increase the recycling of fine sludge and dust disposed normally in landfill, cold bonded pelletizing of the sludge and dust using cement as binder was investigated in laboratory scale as well as in the pilot scale pelletizing plant. The influence of BF flue dust, BOF fine sludge and oily mill scale sludge on the cold strength, capacity and reduction degree of cold bond pellets was studied experimentally on the basis of a statistical procedure. With a coarser representative particle size, oily mill scale sludge has the greatest effect on the cold strength. BF flue dust has a negative effect for increasing both the cold strength and capacity for levels of over 25% of the mixture. The BOF fine sludge has the positive effect on cold strength, while its interaction with BF flue dust has the negative effect on reduction degree.

The results of pelletizing tests in pilot scale show that the maximum cold strength (TTH 94%) and capacity (13–15 t/h) of products is obtained at the conditions given by the optimal mixture design and cure time. The industrial tests on charging cold bonded pellets as burden material in the BOF converter were described. The charging weight of cold bonded pellets varied from 0.5 to 2.5 tons. The results of industrial tests indicated that the converter process was not subject to any adverse disturbances due to the addition of 2.5 tons of cold bonded pellets.

(cf. *ISIJ Int.*, **44** (2004), 770)