

**Fundamentals of High Temperature Processes****Influence of copper on decarburization kinetics of stainless steel melt at high temperatures***H.D.SHIN et al.*

A kinetic study on the decarburization reaction of the Fe–Cr–Cu–C melts has been carried out at 1 873 K focusing on the effect of copper on the reaction rates. The decarburization rate of the Fe–C melt was preliminarily measured at 1 873 K. The result of the present work exhibits a good agreement with other studies. The addition of chromium to the Fe–C melt decreases the interfacial reaction rate. It is considered that the effect of chromium on a retard of the interfacial reaction would have a relationship to the surface adsorption of chromium. The addition of copper to the Fe–Cr–C melt decreases the decarburization reaction rate. The delay of the interfacial reaction by copper at high concentrations of carbon could be responsible for the decrease in the overall reaction rate. The effect of copper on the reaction rate could be quantified by the following equation:

$$k_{\text{Fe-Cr-Cu}} = \frac{k_{\text{FeCr}}}{1 + 0.09[\text{wt}\% \text{Cr}]}$$

From the results of the dependence of the interfacial rates on temperature for each alloy, it could be proposed that the presence of chromium on the reaction surface in the Fe–Cr–C melt would delay the reaction rate, which was originated from the additional reaction steps. However, it is suggested that copper would delay the decarburization rate by blocking a part of the reaction sites in the Fe–Cr–Cu–C melt.

(cf. *ISIJ Int.*, 42 (2002), 809)**Ironmaking****Chemical structure of chars prepared under conditions prevailing in the blast furnace PCI operation***L.LU et al.*

Using a drop tube furnace, char samples were prepared from coals of different ranks, under conditions similar to those prevailing during pulverized coal injection into the blast furnace. The chemical structure of resultant chars was determined by quantitative X-ray diffraction analysis (QXRDA) and high-resolution transmission electron microscopy (HRTEM), and investigated as a function of pyrolysis temperature, heating rate and coal type. Among the parameters examined, pyrolysis temperature was the key factor influencing char chemical structure. Char obtained at higher temperature is generally more ordered, with the distinctive peaks becoming sharper and the background intensity becoming lower. Heating rate is another important factor affecting char chemical structure. Char is more ordered at lower heating rate due to the longer residence time. Although considerable differences were still observed in the chemical structure of chars prepared from coals of different ranks, it is clear that such differences are reduced after coal pyrolysis. Char structural evolution during post-pyrolysis and combustion was also investigated. The importance and potential applications of this work to the blast

furnace PCI operation have been outlined.

(cf. *ISIJ Int.*, 42 (2002), 816)**Characterisation and corrosion of laboratory scale briquettes of reduced iron***J.GRAY et al.*

While considerable work has been reported in literature on the corrosion behaviour and products of direct reduced iron and sponge iron, very little work has been reported on hot briquetted iron, particularly on the effects of the conditions under which the iron ore is reduced and briquetting parameters have on subsequent corrosion behaviour of briquettes.

To investigate this, a laboratory briquetter produced briquettes from finely granulated direct reduced iron (DRI), under pressures up to 160 MPa and at temperatures up to 700°C. Briquetting variables such as heating time, temperature at which compaction takes place, pressure applied and atmosphere under which briquetting took place were all strictly controlled.

Influences of the briquetting parameters of temperature and pressure during compaction on the density and surface area of the HBI were established. Characterised briquettes were then utilised in a study of reoxidation behaviour of hot briquetted iron under various conditions including temperature and salt contamination to simulate storage and transportation related conditions. The studies have established that the influence of reduction and briquetting parameters and the oxidation environment variables of temperature and salt contamination are significant factors in understanding briquette corrosion.

(cf. *ISIJ Int.*, 42 (2002), 826)**Iron ore granulation model supposing the granulation probability estimated from both properties of the ores and their size distributions***N.SAKAMOTO*

It is important to reduce fluctuation of the ore granulation for a stable operation of iron ore sinter plant, because the fluctuation affects directly productivity and productive yield of the operation. To clarify the granulation phenomena in a rotating granulator, an advanced mathematical model that is different from previously proposed ones was developed considering the probability theory. Mathematical characteristics of the model and granulation simulation by the model are summarized as follows:

(1) Since it is difficult to analyze the phenomena by the models based on the motion of quasi-particles due to the complicated movement of large amounts of the quasi-particles, the present model treated it as a kind of probability phenomena.

(2) This model is basically composed of matrix algebras defining following two granulation parameters, 1) overall granulation probability resulted from ore properties, and 2) granulation and disintegration probabilities at each size range of the ores.

(3) This model is useful for evaluation of the granulation phenomena, because the simulation results using the appropriate granulation parameters agree with those from the granulation operation.

(4) It is important to make clear the granulation

conditions for defining the granulation parameters, because the parameters depend on the conditions of the granulation dynamics and the size of the granulator.

(cf. *ISIJ Int.*, 42 (2002), 834)**Flow characteristics in a blast furnace trough***Q.HE et al.*

The aim of this study was to better understand flow characteristics in the taphole stream impingement region of a blast furnace trough, and its effect on localized trough refractory wear. A 1/5th scale perspex model was used, and oil and water were adopted to simulate the molten iron and slag, respectively. Velocities and turbulence intensities in the region adjacent to the trough wall were measured by means of laser doppler velocimetry (LDV). This study highlighted the entrainment of bubbles by the impinging taphole stream, resulting in a buoyancy-driven flow pattern within the trough. The identified buoyancy-driven flow resulted in high velocities and turbulence intensities in the region where maximum refractory wear occurred. Methods for minimizing the influence of the buoyancy-driven flow, and resultant high velocities and turbulence intensities are proposed in this paper.

(cf. *ISIJ Int.*, 42 (2002), 844)**Steelmaking****Dissolution rate of Al<sub>2</sub>O<sub>3</sub> into molten CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags***J.-Y.CHOI et al.*

The dissolution rate of Al<sub>2</sub>O<sub>3</sub> into the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slag system was investigated at 1 873 K by employing a novel experimental method which involved continual measurement of the torque variation on a rotating alumina rod dipped into a molten slag. Measured torque variation was successfully related to the dissolution rate of the rod. The dissolution rate of alumina was found affected by a number of factors: the rate increased with increasing temperature, the rotating speed of the rod, the CaO content in the slag, and the Al<sub>2</sub>O<sub>3</sub> content in the slag for a fixed CaO content. It was found that the dissolution rate was highly dependent on the viscosity and the diffusivity of slags. The activation energy obtained from an Arrhenius type analysis was in the range of 84 kJ mol<sup>-1</sup>. It was concluded that the dissolution of Al<sub>2</sub>O<sub>3</sub> into the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slag system was controlled by the mass transfer in the slag phase. An iso-dissolution rate diagram was constructed for the dissolution of Al<sub>2</sub>O<sub>3</sub> into the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slag system at 1 873 K.

(cf. *ISIJ Int.*, 42 (2002), 852)**Effect of bottom nozzle arrangement on splashing and spitting in combined blowing converter***T.M.J.FABRITIUS et al.*

Wear of refractory lining, skulling of converter cone and metal losses were studied by splashing and spitting measurements in physical model during combined blowing. The aim of the present study was to determine the effect of the bottom nozzle

arrangement and lance height as far as on harmful splashing and spitting in combined blowing converter are considered. The investigation has concentrated mainly on the initial period of blowing.

According to the model tests, total splashing on the converter walls increases as a function of number of bottom nozzles (with increase of total gas flow rate) both initial and final period of blowing. At the initial period of blowing, combined blowing produces maximum measured total splashing and large reaction area as a form of droplets. The nozzles arranged at the centre of the vessel increase metal losses and skulling of the converter cone especially with lowered lance height. The introduction of outside of lance cavities arranged bottom nozzles decreases metal losses and skulling of converter cone compared to the top lance blowing at final period of blowing. The usage of high lance height and several bottom nozzles accelerate wear of the refractory, especially at the knuckle area and charge pad area. It is possible to reduce splashing to the knuckle areas with certain lance gaps by positioning bottom nozzles directly between the cavity and knuckle area with remarkable (approximately 30–40%) overlap.

(cf. *ISIJ Int.*, **42** (2002), 861)

### Forming Processing and Thermomechanical Treatment

#### Three-dimensional numerical analysis of microstructural evolution in and after bar and shape rolling processes

J. LIU *et al.*

An integrated numerical model predicting microstructural evolution, three-dimensional plastic deformation and temperature changes has been applied to industrial hot bar rolling and H-beam rolling. This model enables us to predict three-dimensional metal flow and temperature changes as well as transient in grain size change and dislocation density distribution in and after hot rolling. To demonstrate the successfulness of the proposed model, it was applied to the analysis of two different industrial bar rolling schedules, in which total number of passes and caliber systems were different with each other. It was also applied to the analysis of the H-beam rolling sequences with different heat treatment conditions. Microstructural evolution starting from deformed austenite to ferrite/pearlite/bainite after phase transformation was successfully simulated. Microstructural evolution in and after hot rolling as well as metal flow and temperature can be easily obtained through the proposed model using rolling condition and alloy composition as the functional variables. This model is a very useful tool for designing and optimizing rolling conditions so that products with the best internal quality and dimensional accuracy can be obtained.

(cf. *ISIJ Int.*, **42** (2002), 868)

### Welding and Joining

#### Weldability of galvanized interstitial free steel

C.A. CAMPOS *et al.*

A series of interstitial free steel strips were sub-

jected to different annealing treatments after being galvanized by immersion. Samples from these strips were cut and various tests were carried out on them. The coating was studied by optical and scanning electron microscopy, analysis of the X-ray spectra was conducted on the samples while being observed in the latter equipment. Resistance to powdering of the coating was studied by means of V-bend testing. Spot resistance welding tests were conducted by varying the current supplied by the machine, different geometrical parameters and the resistance of the welded joint were evaluated. It was found that the amount of powdering of the coating increased as the amount of  $\Gamma$  phase augmented, as well as with the increment in coating thickness. The mechanical strength of welded strips was found to improve with the increment in welding current, up to the point where expulsion of material was occurred.

(cf. *ISIJ Int.*, **42** (2002), 876)

### Transformations and Microstructures

#### Microstructural evaluation of C-free martensitic alloys at high temperatures

K. YAMADA *et al.*

Microstructure of C-free martensitic alloys at elevated temperatures was studied for understanding the origin of their superior creep properties over 923 K. These alloys initially have martensitic structure and the heterogeneous creep deformation seems to be suppressed even under low stress region in distinction from the conventional heat resisting steels because there is no rapid growth of carbides during creep at high temperatures.

Inter-metallic compounds such as Laves or  $\mu$  phase were dominantly observed over 923 K and these precipitation had been followed by the low temperature reaction that greatly contributed to the typical aging behavior like in the usual maraging steels. It was found that the density of the precipitation was still kept high even at 973 K because its gathering and coalescence rate was small comparing with that of high Cr steels. Furthermore, the reversely transformed austenite phase certainly appeared by the shearing mechanism in these alloys when the materials were rapidly heated up to the temperature for creep testing, because their  $A_s$  points were measured to be at around 873 K. This austenite phase represented terrace like feature in SEM observations. Fortunately, this characteristic structure was resulted from a selective electro-polishing in specimen preparation due to the compositional fluctuation. However, it was also confirmed that partitioning of alloying element was not completed in the short-term aged materials.

It was concluded that the characteristic microstructure of these alloys over 923 K was continuously formed as follows. Firstly, uniform fine precipitation of inter-metallic compounds occurred at early stage and then the reversely transformed austenite was broken out without diffusion process. Finally, dissolution of precipitation in the retained martensitic region was assisted by long-term keeping at high temperatures. Consequently, it was expected that specific creep resistance of these alloys over 923 K be achieved by existence of large amount

of austenitic phase strengthened by fine precipitation.

(cf. *ISIJ Int.*, **42** (2002), 882)

#### Precipitation and recrystallization behavior in extra low carbon steels

J.-Y. CHOI *et al.*

Effects of precipitation on the recrystallization behavior of two Ti-added extra low carbon sheet steels were compared. The recrystallization temperature of the higher Ti-containing steel is higher than that of the lower Ti-containing steel. Small Angle Neutron Scattering (SANS) technique revealed no additional carbo-nitrides precipitation during the recrystallization annealing procedure in the low Ti-containing steel. However, in higher Ti-containing steel, new TiC precipitates, with a size range of several nm to several tens of nms, form during the recrystallization annealing process. This dynamic interaction of the precipitation of fine TiC particles with the recovery of dislocations seems the primary source of the retardation of the recrystallization in the higher Ti-containing extra low carbon steel.

(cf. *ISIJ Int.*, **42** (2002), 889)

#### Determination of Ms temperature in steels: A bayesian neural network model

C. CAPDEVILA *et al.*

The knowledge of the martensite start (Ms) temperature of steels is sometimes important during parts and structures fabrication, and it can not be always properly estimated using conventional empirical methods. The additions in newly developed steels of alloying elements not considered in the empirical relationships, or with compositions out of the bounds used to formulate the equations, are common problems to be solved by experimental trial and error. If the trial process was minimised, cost and time might be saved. This work outlines the use of an artificial neural network to model the calculation of Ms temperature in engineering steels from their chemical composition. Moreover, a physical interpretation of the results is presented.

(cf. *ISIJ Int.*, **42** (2002), 894)

#### Texture development during dynamic recrystallization in hot-deformed Fe-40at%Al alloy

T. SAKATA *et al.*

Microstructure and crystal orientation distribution in hot-compressed Fe-40at%Al alloy were investigated using an electron back-scatter diffraction pattern technique. After the hot deformation, grain boundaries became more serrated with increasing tested temperature or decreasing strain rate, *i.e.*, decreasing the Zener-Hollomon parameter ( $Z$ ). Equiaxed fine grains surrounded by high angle boundaries were homogeneously formed due to dynamic recrystallization accompanied by serrated grain boundaries during hot deformation at lower  $Z$ . Moreover, strong (111) fiber texture parallel to the compressive axis developed at larger strains because of the lattice rotation during hot deformation, which was good agreement with the stable orientation calculated by Taylor model. The microstructural fac-

tors which established the mechanism of texture evolution during dynamic recrystallization were examined focusing on the  $Z$  parameter.

(cf. *ISIJ Int.*, **42** (2002), 903)

## Mechanical Properties

### Ductility and formability of newly developed high strength low alloy TRIP-aided sheet steels with annealed martensite matrix

*K.SUGIMOTO et al.*

Formable high-strength low-alloy TRIP-aided sheet steels with annealed martensite matrix or "TRIP-aided annealed martensitic steel" were developed for automotive applications. The steels possessed a large amount of plate-like retained austenite along annealed martensite lath boundary, whose stability against the strain-induced transformation was higher than that of the conventional "TRIP-aided dual-phase steel" with polygonal ferrite matrix. In a tensile strength range between 600 and 1000 MPa, the TRIP-aided annealed martensite steels exhibited a superior large elongation and reduction of area. In addition, they possessed the same excellent stretch-flangeability and bendability as "TRIP-aided bainitic steel" with bainitic ferrite matrix. These properties were discussed by matrix structure, a strength ratio of second phase to matrix, retained austenite stability, internal stress and so on.

(cf. *ISIJ Int.*, **42** (2002), 910)

### Effect of Nb on the proof strength of ferritic stainless steels at elevated temperatures

*A.MIYAZAKI et al.*

The effect of Nb on the high temperature proof strength of 0.46% Nb-added ferritic stainless steel was studied from the viewpoints of solid solution strengthening, precipitation strengthening, and precipitation strengthening during tensile test and/or preceding hold time. The results obtained were as follows.

(1) The increase in high temperature proof

strength in Nb-added ferritic stainless steel is particularly remarkable at around 700°C in comparison with that in Ti-added steels.

(2) After aging treatment for 2 h at 700°C, in addition to the approximately 0.14% content of coarse Nb carbides and nitrides which had precipitated before this aging treatment, fine Fe<sub>2</sub>Nb Laves phase particles with a size of 0.02 μm precipitated out in an amount of approximately 0.3%, and virtually no solid solution Nb existed in the steel. The 700°C proof strength in this condition showed a value near the 700°C proof strength before the aging treatment, that is, when approximately 0.3% solid solution Nb was present.

(3) When aging treatment is performed at 700°C for 2 h or more, virtually all the added Nb precipitates out. The coarsening of the Fe<sub>2</sub>Nb Laves phase particles within the range of 0.02–0.05 μm during aging at 700°C greatly decreases the high temperature proof strength at 700°C.

(4) Cold rolled steel sheets of Nb-added ferritic stainless steel are normally manufactured by annealing at a temperature of 900°C or higher in order to cause recrystallization. Accordingly, before measurement of the proof strength at 700°C, the steel contains a large quantity of solid solution Nb. The phenomenon of particularly high strength at 700°C is considered to be attributable to the precipitation of this solid solution Nb as a fine Fe<sub>2</sub>Nb Laves phase during the tensile test and/or preceding hold time.

(cf. *ISIJ Int.*, **42** (2002), 916)

## Social and Environmental Engineering

### Dissolution behavior and stabilization of fluorine in secondary refining slags

*H.SUITO et al.*

Dissolution of fluorine in secondary refining and synthetic CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–(P<sub>2</sub>O<sub>5</sub>) slags has been studied by using the shaking test and its behavior is discussed based on the results for the time dependence of Ca, Si, Al and F contents in aqueous solution. It was found that fluorine dissolution is affect-

ed by the contents of SiO<sub>2</sub>, F and total Fe in slag and particularly its effect is obvious in synthetic slags. The dissolved fluorine from slags with low contents of SiO<sub>2</sub> and total Fe can be immobilized through the incorporation of fluorine into precipitated hydrates such as CaO–Al<sub>2</sub>O<sub>3</sub>–H<sub>2</sub>O compound and CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–H<sub>2</sub>O gel. In the case of slags with high SiO<sub>2</sub> and low total Fe contents, the dissolved fluorine can be immobilized through the formation of CaO–SiO<sub>2</sub>–H<sub>2</sub>O–SO<sub>4</sub>–F gel by the addition of gypsum to aqueous solution. The dissolution behavior of fluorine in seawater has been also studied.

(cf. *ISIJ Int.*, **42** (2002), 921)

### Influence of gypsum addition and hydrothermal treatment on dissolution behavior of fluorine in hot metal pretreatment slags

*R.INOUE et al.*

Immobilization of fluorine by using calcium aluminate, calcium silicate, calcium aluminum silicate and secondary refining slag as a stabilizing agent has been studied by focusing on the effect of gypsum addition on fluorine dissolution from hot metal pretreatment slags in shaking test. When gypsum is added to aqueous solution in which calcium aluminate or secondary refining slag with low contents of both SiO<sub>2</sub> and total Fe are present, fluorine immobilization does not occur due to the formation of ettringite and monosulfate on particle surface of added stabilizing agent. In the case of the mixture of calcium silicate and gypsum, calcium aluminum silicate or secondary refining slag with high SiO<sub>2</sub> and low total Fe contents, fluorine ion in solution can be immobilized through the formation of C–S–H–F–SO<sub>4</sub> gel, Ca<sub>10</sub>(SiO<sub>4</sub>)<sub>3</sub>(SO<sub>4</sub>)<sub>3</sub>(OH,F)<sub>2</sub> and Ca<sub>5</sub>[(Si,S)O<sub>4</sub>]<sub>3</sub>(OH,F). It was found that fluorine is immobilized by hydrothermally treating the mixture of hot metal pretreatment slag, secondary refining slag with high SiO<sub>2</sub> and low total Fe contents and gypsum at 80°C for 3 h.

(cf. *ISIJ Int.*, **42** (2002), 930)