（＊掲載記事題目及び掲載頁は変更になる場合があります。）

Fundamentals of High Temperature Processes

Contributions by Japanese researchers at Carnegie Mellon University (Review)

R.J.FRUEHAN

A significant amount of valuable fundamental research has been conducted by Japanese researchers at the Center or Iron and Steelmaking Research (CISR) at Carnegie Mellon University. The work of these researchers, with the author, are reviewed in this paper. Research on ironmaking, steelmaking and refining is included. Examples include fundamentals of iron smelting, refining for phosphorus and nitrogen, slag foaming and the kinetics of various gas–metal reactions.

(cf. *ISIJ Int.*, **45** (2005), 1221)

Empirical expression of phosphorus solubility in molten $Fe_{1-y}Cr_y$ given as functions of temperature and phosphorus activity

N.SHOHOJI et al.

Chemical activity–temperature–composition (a–T–x–y) relationships determined by Knudsen effusion technique were made available for molten Fe–Cr–P system by a group of Russian researchers. Nevertheless, they were not presented in form of solubility x in $Fe_{1-y}Cr_yP_x$ as explicit functions of phosphorus activity a_P and temperature T for given y and thence they are not readily usable for evaluating P solubility in molten $Fe_{1-y}Cr_y$ at arbitrary T under certain a_P. In the present work, effort was invested to derive empirical expression for the solubility x in $Fe_{1-y}Cr_yP_x$ as functions of T and a_P at given y from the reported a_P–T–x–y relationships in discrete tabulated format. Such analytical expression of solubility x might allow us to proceed with more profound consideration for atomic interaction and atomic configuration in the molten $Fe_{1-y}Cr_yP_x$ on the basis of statistical thermodynamics.

(cf. *ISIJ Int.*, **45** (2005), 1226)

Microwave heating behavior of blast furnace slag bearing high titanium

C.YAN et al.

Blast furnace (BF) slag in south-western part of China contains large amount of titanium. For the purpose of beneficial utilization of titanium in the slag, microwave (MW) processing of the slag has been proposed. In this study, a fundamental research on heating behavior of the slag by application of 2.45 GHz MW was performed.

The slag specimens can be heated in a domestic MW oven at constant input power (0.5 kW) and sudden increase of the temperature is observed after several heating cycles. A phenomenon of so-called thermal runaway (TRW) occurred. A part of the specimen melted, and the XRD analysis indicated that this area became amorphous. Crystallization of the $CaTiO_3$ phase occurred by MW heating of the melted slag at 600°C.

A sintered $CaTiO_3$ compact was heated by MW much more than the synthetic Chinese slag. The synthetic slag without containing Ti was not heated very well. Permittivity of $CaTiO_3$ (loss factor) was measured and demonstrated to be much larger than the other oxides in the slag. Therefore, it is concluded that $CaTiO_3$ phase is responsible for heating of the whole slag.

(cf. *ISIJ Int.*, **45** (2005), 1232)

Precipitation and growth of V-concentrating phase in synthetic V-bearing steelmaking slag

Y.DONG et al.

The precipitation and growth of V-concentrating phase are implemented in the synthetic V-bearing steelmaking slag based on the composition of factory slag from the Masteel Co. X-ray diffraction (XRD) and scanning electron microscopy (SEM), with energy dispersive X-ray spectrometer (EDX) are used to investigate the slag after heat treatment and to determine the temperature at which crystallization of V-concentrating phase is initiated. It is demonstrated Whitlockite with a high content of V_2O_5 (called V-concentrating phase) nucleates homogeneously and heterogeneously at 1 623–1 598 K. When emplaced holding time at 1548K, the crystals of V-concentrating phase grow with increasing of the holding time using crystal size distribution theory (CSD). Observation of the microstructures and crystallite-size data indicates that the precipitation of V-concentrating phase proceeds *via* three different mechanisms: nucleation, growth, and coalescence of grains of V-concentrating phase.

(cf. *ISIJ Int.*, **45** (2005), 1238)

Solubility of oxygen in iron–silicon melts in equilibrium with silica at 1 873 K

S.S.SHIBAEV et al.

The solubility of oxygen in iron-silicon melts in equilibrium with silica was measured within the range from 0.1 up to 70 mass% Si at 1 873 K. The experimental procedure involved alloys melting in silica crucibles under argon atmosphere. The sampling was made by melt sucking into quartz tubes, equipped with copper chillers. The oxygen content of analytical samples was determined with inert gas fusion analysis after careful sample preparation. The results obtained were treated by thermodynamic model, which allowed to calculated the activity and solubility of oxygen in Fe–Si melts up to 100 mass% Si.

The isotherm of oxygen solubility exhibits both intermediate minimum and maximum at 20 and 85 mass% Si, respectively. The corresponding values of oxygen saturated contents are as follows: 1.4 and 94 μg/g. The activity coefficient of oxygen shows alternating deviations from the additive behaviour. These are positive in the iron rich melts, containing up to 45 mass% Si. In the melts with higher silicon content the deviations from additivity are negative. The following values of interaction parameters were calculated: $\varepsilon^{Si}_{O(Fe)} = 12.9 \pm 2.7$ and $\varepsilon^{Fe}_{O(Si)} = -6.5 \pm 2.0$.

(cf. *ISIJ Int.*, **45** (2005), 1243)

Characterisation of manganese furnace dust and zinc balance in production of manganese alloys

R.SHEN et al.

Manganese furnace dust is made up of volatiles and raw materials fines collected from the off-gas during smelting of manganese alloys. Currently, manganese furnace dust is accumulated in large settling ponds. Major factors preventing recycling of the manganese furnace dust to the ferroalloy furnaces are handling, due to its tar content, and accumulation of zinc in the furnaces, which can cause irregularities in their operation. This paper presents characteristics of manganese furnace dust generated in ferromanganese and silicomanganese production at Tasmanian Electrometallurgical Company and analyses zinc balances in light of furnace dust recycling. If manganese furnace dust is recycled to the ferroalloy furnaces *via* the sinter plant, the overall zinc input will increase by 51–143 % depending on charging materials.

(cf. *ISIJ Int.*, **45** (2005), 1248)

Ironmaking

Kinetic analysis of the iron oxide reduction using hydrogen–carbon monoxide mixtures as reducing agent

A.BONALDE et al.

The kinetics of the reduction of hematite pellets using hydrogen–carbon monoxide mixtures as reducing agent was described by using the "grain model". This model involves the particle size and the porosity of the pellet as main structural parameters which affect directly the kinetics of the hematite pellets during the reduction process. The predictions of the model were compared with the experimental results. Fired hematite pellets were reduced at 850°C using hydrogen, carbon monoxide and Midrex gas. The weight loss technique was used to follow the reduction process. The reduction of iron oxide pellets using hydrogen or carbon monoxide is a mixed controlled system, where chemical reaction and internal gas diffusion are competing processes during the first stage of the reduction, while internal gas diffusion becomes controlling step at the last stage of the process. The reduction of iron oxide pellets using Midrex gas is a mixed controlled system throughout the whole reduction process.

(cf. *ISIJ Int.*, **45** (2005), 1255)

Interfacial phenomena occurring during Iron/Char interactions in a blast furnace

F.MCCARTHY et al.

Using the sessile drop approach, interfacial reactions taking place in the iron/carbon interfacial region were investigated at 1 550°C in a horizontal tube resistance furnace with an argon atmosphere. Two coal-chars, labelled as 1 and 2 with respective ash concentrations of 10.88 wt% and 9.04 wt%, and electrolytically pure iron were used in this study. Liquid iron droplets were exposed to chars at high temperatures for times ranging between 1 to 180 min and the assembly was then withdrawn into the colder section quenching the droplet. To examine the time dependant growth of new phases formed in the interfacial region, FESEM and EDS investigations were carried out on the underside of the droplet, which effectively represents the iron/char interface. The transfer of carbon and sulphur into the iron droplet was also determined using a LECO Analyser. Inter-

facial regions for both chars showed a high occurrence of ash deposits, which were found to increase with time. Al, Ca, S, O, Fe were also detected in EDS analysis of the interface. However very low levels of Si were found in the interfacial region despite high concentrations of silica in the chars initially suggesting chemical reactions involving silica. After three hours of contact, carbon pick-up by liquid iron reached only 0.12 wt% and 0.28 wt% for Char 1 and Char 2 respectively, both of which were much below the saturation level of 5.6 wt%. These results are discussed in terms of the formation of interfacial products, the consumption of solute carbon by reducible oxides and low intrinsic rates of carbon dissolution from non-graphitic Chars.

(cf. *ISIJ Int.*, **45** (2005), 1261)

Time-dependent fractal characteristics on time series of Silicon content in hot metal of blast furnace

C.H.GAO et al.

The fractal analysis of data on silicon content in hot metal obtained in No. 1 blast furnace at Laiwu and No. 6 blast furnace at Linfen Iron and Steel Group Co. respectively is performed using power spectrum method to examine the possible scale-invariance laws. The results confirm the existence of fractal characteristics in the investigated time series, which provides a powerful tool to explore complex blast furnace system and makes the application of fractal theory to blast furnace full of potential and attraction.

(cf. *ISIJ Int.*, **45** (2005), 1269)

Three-dimensional simulation of flow and combustion for pulverised coal injection

B.GUO et al.

A three-dimensional numerical model of pulverised coal injection has been developed for simulating coal flow and combustion in the tuyere and raceway of a blast furnace. The model has been used to simulate previously reported combustion tests, which feature an inclined co-axial lance with an annular cooling gas. The predicted coal burnout agrees well with that measured for three coals with volatile contents and particle size ranging between 20.2–36.4% and particle sizes 1–200 μm. Many important phenomena including flow asymmetry, recirculating flow and particle dispersion in the combustion chamber have been predicted. The current model can reproduce the experimental observations including the effects on burnout of coal flowrate and the introduction of methane for lance cooling.

(cf. *ISIJ Int.*, **45** (2005), 1272)

Steelmaking

Kinetics of oxygen refining process for ferromanganese alloys

Y.E.LEE et al.

The present analysis of the experimental data by Yamamoto *et al.* permitted to determine the rate controlling mechanisms for the decarburization and evaporative manganese loss concurrently taking place during the oxygen refining process of ferromanganese melt.

When oxygen is supplied by a top lance blowing mode, the decarburization reaction takes place by three different mechanisms in sequence. The chemical reaction at the melt-gas interface controls the rate of decarburization during the first period, the rate of oxygen supply through the boundary layer in gas during the second period, and the mass transfer rate of carbon in melt during the third period when the carbon content is less than 2 mass%.

Manganese is lost primarily by evaporative reaction, but its dynamics are affected by the prevailing excess oxygen after accounting for CO formation. The excess oxygen and manganese vapor establish counter-current flux and form MnO mist at some distance away from the metal–gas interface. This creates two diffusion boundary layers, one for the flux of manganese vapor adjacent to the melt–gas interface and the other for the flux of excess oxygen in the gas phase. When the vapor pressure of manganese at the metal–gas interface is low, the rate of manganese vapor loss is controlled by the flux of excess oxygen. Otherwise, it is determined by the flux of manganese vapor.

(cf. *ISIJ Int.*, **45** (2005), 1282)

Casting and Solidification

Mathematical heat transfer model research for the improvement of continuous casting slab temperature

H.WANG et al.

To improve the temperature of continuous casting slab, a mathematical heat transfer model simulating the solidification process of continuous casting slab was developed based on the technical conditions of the slab caster of Steelmaking plant of Wu-Han Iron and Steel Group Corp., by which the slab temperature distribution and shell thickness were computed. The adequacy of the model was compared with the measured slab surface temperature at the caster exit. The effects of the main operation parameters including casting speed, secondary cooling conditions, slab size and steel melt superheat on the solidification process were discussed and the means of enhancing the slab temperature was brought forward. Raising the casting speed from 1.0 or 1.1 to 1.3 m/min, controlling the flow rate of secondary cooling water and optimizing the spray pattern at the lower segments of secondary cooling zone could effectively improve the slab temperature. Whereas increasing the superheat is adverse to the production of slab with high temperature. The results of model research have been applied to plant operation at Steelmaking plant of Wu-Han Iron and Steel Group Corp. The slab surface temperature has risen from 900 to 1 250°C, and the slab are directly fed to the rolling mill after exiting caster.

(cf. *ISIJ Int.*, **45** (2005), 1291)

Application of bismuth for solidification structure refinement and properties enhancement in as-cast high-speed steels

A.S.CHAUS

In order to exhibit good all-round performance the impact toughness enhancement of as-cast high-speed steels is obligatorily needed. In general, different methods are used commercially to achieve cast structure refinement and, as a consequence, their properties are improved. Introduction into the melt of inoculant particles or surface-active additions is among most beneficial. However, the effect of modifying additions in as-cast high-speed steels has been studied insufficiently. In fact, a restricted number of modifiers is used for structure and properties improvement in the as-cast high-speed steels compared to the common cast alloys. In the present work several kinds of alloys including tungsten-molybdenum high-speed steels of M2 and T30 types and low-alloy tungsten-free 1.1C–5Mo–1.7V high-speed steel were melted to investigate the effect of bismuth on their structures and properties.

It has been found that additions of bismuth produce a very fine cast structure and affect the shape of the matrix grains and the morphology of the eutectic carbides as well as the redistribution of the main alloying elements of high-speed steels between solid solution and eutectic carbides. The microstructural changes, induced by bismuth during solidification, are explained by the surface activity of bismuth, which segregates to liquid/solid interface, significantly blocking dendrite growth in the direction along certain crystallographic planes. It has been shown that during eutectic solidification, carbides are also exposed to the barrier effect of bismuth being surrounded in the melt by this element. The main metallographic features of the modified cast structure alongside with the purifying effect produced by bismuth are retained after full heat treatment affecting the final mechanical properties of as-cast high-speed steels. As a result, bismuth significantly increases impact toughness and wear resistance of as-cast high-speed steels but decreases their red hardness.

(cf. *ISIJ Int.*, **45** (2005), 1297)

Forming Processing and Thermomechanical Treatment

Influence of the size and volume fraction of TiN particles on hot strength and dynamic recrystallisation in structural steels

S.F.MEDINA et al.

The low solubility of titanium nitrides (TiN) in austenite is taken advantage of in structural steels to control the evolution of the microstructure in the hot rolling process and in the heat affected zone (HAZ) in processes involving the application of heat, such as welding. However, the quantitative influence of the precipitation state of these particles on hot strength and dynamic recrystallisation kinetics, given by the precipitate size distribution and the precipitated volume, is practically unknown. The present work studies the influence of various Ti and N compositions, which give rise to different precipitation states at the reheating temperatures, on the aforementioned phenomena. The influence of the precipitation state on hot strength has been quantified by changes in the peak stress and the activation energy. A maximum has been obtained for the activation energy which corresponds to a Ti/N ratio of

approximately 1.3. The model used to predict the flow curve and dynamic recrystallisation kinetics has been improved, extending it to include microalloyed steels containing Ti.

(cf. *ISIJ Int.*, **45** (2005), 1307)

Analysis of the effect of tension at the entry of cold rolling mill on the stability of strip tracking

T.TARNOPOLSKAYA et al.

Strip track-off, particularly at high speed, is a serious operational problem that could lead to mill crashes and damaged rolls. It predominately occurs at the entry of the tandem cold mill, where the entry tension is relatively low. This paper presents an analysis of the effect of entry tension on the stability of strip tracking in the first stand of a cold rolling mill using a recently developed mathematical model of strip lateral dynamics in cold rolling. The analysis reveals that the entry tension is a crucial parameter in stabilizing the strip tracking if buckling of the strip is present. A procedure of selecting the entry tension that ensures stable strip tracking for a given mill schedule is discussed.

(cf. *ISIJ Int.*, **45** (2005), 1316)

Welding and Joining

Abrasive wear behaviour of Fe–30Cr–3.6C overlays deposited on mild steel

T.SHARMA et al.

This paper describes the influence of sliding wear conditions and post weld heat treatment on abrasive wear resistance of iron base hardfacing overlays (Fe–30Cr–3.6C) deposited on mild steel. Overlays were deposited by a shielded metal arc (SMA) welding process on mild steel using a commercially available hardfacing electrode (Sugar-Arc) of 4.0 mm in diameter. Overlays were deposited using a welding current of 250 A (DCEN) and welding speed of 15 cm/min. The abrasive wear resistance of overlays in as-welded and heat-treated condition was tested using a pin on disc type wear testing machine against a 320 grade SiC abrasive paper at different normal loads (1–4 N). Optical microscopy was used to study the microstructure of overlays. Scanning electron microscopy (SEM) wear surfaces was carried out to analyze the wear mechanism. Variation in the hardness across the coating substrate interface of was observed. Post weld heat treatment improved the abrasive wear resistance.

(cf. *ISIJ Int.*, **45** (2005), 1322)

Surface Treatment and Corrosion

A zinc and manganese phosphate coating on automobile iron castings

G.-Y.LI et al.

A modified phosphate coating on automobile iron castings was described in this paper. The phosphating bath was modified by adding sodium molybdate. The microstructure of the phosphate coating was remarkable refined as the addition of Na_2MoO_4 increases to 1.5–2.0 g/L. As a result, the corrosion current of the coatings measured by electrochemical polarization decreases as Na_2MoO_4 increases, which indicates the increase of the corrosion-resistance of the coatings. The modified phosphate coating was used to automobile castings as an intermediate protect layer before final painting. It was shown that the coating containing molybdate can improve the adhesion of painting onto the automobile casting. Salt spray test and atmospheric corrosion test indicated that the anticorrosion performance of the paint plus phosphate coatings on automobile castings was also improved significantly.

(cf. *ISIJ Int.*, **45** (2005), 1326)

Effects of S content and surface finish on pitting corrosion of austenitic stainless steels containing Mo in chloride and bromide solutions

M.KANEKO et al.

Pitting corrosion behavior of austenitic stainless steels with Mo was investigated in chloride and bromide solutions. The steels with higher S content as 0.009 mass% showed higher pitting potential in 1 kmol/m^3 bromide solution than 1 kmol/m^3 chloride solution. On the other hand, the steels with lower S content as 0.0003 mass% showed opposite results. The higher pitting potential was observed in chloride solution. This tendency became profound with passivation treatment by nitric acid. From the experimental results above, it is highly believed that chloride ions are more detrimental to sulfide inclusions induced pitting than bromide ions, whereas pitting due to breakdown of passive film other than sulfide inclusion is more easily caused in solutions containing bromide ions than chloride ions.

(cf. *ISIJ Int.*, **45** (2005), 1331)

Transformations and Microstructures

Numerical simulation of copper precipitation during aging in deformed Fe–Cu alloys

J.YANG et al.

A numerical model was developed to simulate the competing precipitation of Cu particles on dislocations and in the matrix in Fe–Cu alloys. The nucleation and growth rates and the remaining Cu concentration in the matrix were calculated successively at a large number of fine discrete time steps. In the absence of dislocations the results of precipitation in the matrix that was assumed to occur homogeneously were in essential agreement with those of Langer–Schwartz (L-S) model and Lifshitz–Slyozov–Wagner (LSW) coarsening theory. The heterogeneous precipitation on dislocations was incorporated taking into account the development of solute-depleted zone around dislocations. The coarsening behavior of particles on dislocations and in the matrix deviated substantially from those of previous theories probably due to the interaction of diffusion fields between heterogeneous and homogeneous precipitation zones. In other words, coarsening can occur at the expense of smaller particles nucleated in the matrix at late stages. The bcc to fcc transformation of Cu particles that occurs during growth was likely to accelerate the coarsening of Cu particles. The simulation results agreed well with experiment in respect of the particle number and mean particle radius, but the model yielded a considerably narrower particle size distribution than experiment reported in the literature.

(cf. *ISIJ Int.*, **45** (2005), 1335)

Mechanical Properties

Modeling the effect of copper on hardness of microalloyed dual phase steel through neural network and neuro-fuzzy systems

S.K.GHOSH et al.

The effects of copper along with some microalloying elements and the processing parameters are modeled with artificial neural network and adaptive neuro-fuzzy inference system. Both the tools are found to be useful for modeling the effect of copper and other alloying additions along with the processing parameters on the hardness of microalloyed DP steels. In case of the neural network, the proposed committee of models is found to be effective in handling the problem of mapping the input-output relation in these steels. The increase in the number of rules is found to improve the predictability of the neuro-fuzzy inference system. The predictions made by both the models substantiate the knowledge of physical metallurgy principles.

(cf. *ISIJ Int.*, **45** (2005), 1345)

Comparison of cold formability of cold drawn non-heat-treated steels having similar strength

K.S.PARK et al.

The cold formability of the drawn non-heat-treated steels, *i.e.* dual phase (DP) steel, low Si steel and ultra low carbon bainitic (ULCB) steel, was examined in terms of the deformation resistance and the forming limit. The present investigation was aimed at elucidating the effect of drawing on the cold formability of non-heat-treated steels which is directly affected by drawing since no heat treatment are involved during forming processes for them. A special care was taken for the present steels to exhibit the similar strength after drawing, so eliminating the strength effect. The present steels after drawing revealed the elastic-near perfect plastic behavior in compression. After drawing, the low Si steel exhibited the lowest deformation resistance estimated by the absorbed energy during deformation. In case of the forming limit in terms of the critical strain under which no cracking occurs during the upsetting test of the drawn steels, the low Si steel and the ULCB steel were better than the conventional heat-treated steel. Accordingly, among several non-heat-treated steels which can replace the conventional heat-treated steel as forging steels, the low Si steel seems to exhibit the best performance if they have the similar strength. The compressive deformation behavior of the present drawn non-heat-treated steels was discussed in association with the strain hardened state and the Bauschinger effect developed by drawing. In addition, their cold formability was explained by the plastic incompatibility between the constituent phases of each steel.

(cf. *ISIJ Int.*, **45** (2005), 1352)

Social and Environmental Engineering

Metallurgical investigations on two sword blades of 7th and 3rd century B.C. found in Central Italy

W.NICODEMI et al.

This study aims at casting new light about the knowledge of the metallurgical techniques developed by the Etruscan and the Romans during their political and cultural interactions in Central Italy. The analysis of two weapons found at the Etruscan sites of Vetulonia and Chiusi have pointed out some new information about the production process performed. The optical microscopy analysis has allowed to identify the sequence of the constituent microstructure present in the two ancient weapons. SEM-EDS has permitted to identify the chemical composition of the non metallic inclusion and to estimate the average temperature of the reduction process. The analysis of the metal matrix performed by a coupled argon plasma spectrometer permitted to measure the average chemical compositions of the studied alloys. SEM-EBSD analysis has allowed to identify the crystallographic textures present within the different zones of the sword blades and this has indicated the realization of a forming process that gave interesting mechanical properties to the metal products. The results obtained by the Etruscans artisans were of very high standard quality and their production system had been certainly assimilated by the Romans who found in them a strategic factor to increase their power.

(cf. *ISIJ Int.*, **45** (2005), 1358)