Fundamentals of High Temperature Processes

High power ultrasonics in pyrometallurgy: Current status and recent development (Review)

S.V. KOMAROV et al.

In recent years, a large number of studies have been published on the use of high intensity ultrasonics in various high temperature technologies. This paper provides an overview of the recent achievements and ongoing works on the application of high intensity sound waves to pyrometallurgy and its related areas. The published results have strongly suggested that ultrasonics has the potential to play a more significant role in such areas as the dedusting of high-temperature exhaust gas, improvement of fuel-combustion efficiency, control of air-pollutant emissions, improvement of the quality of ingots, production of metal powders and as-cast composite materials.

At higher temperatures, special attractiveness of sound waves is associated with the fact that the waves can propagate through gas, liquids, and solids, and thus supply the acoustic energy from a cooled sonic generator to materials being processed under high temperature conditions. This provides a unique tool, for example, for controlling the rates of interfacial phenomena that is unachievable by any other methods under high temperatures.

Industrial competitiveness of the ultrasonic-based technologies is reinforced by the relatively low cost of power-generating equipment and ultrasonic transducers. However, further research efforts are called for to develop new heat-resistant waveguide materials and to integrate the ultrasonic installations with existing industrial facilities in high temperature technologies.

(cf. *ISIJ Int.*, **45** (2005), 1765)

Deoxidation equilibrium of chromium in liquid Iron-Nickel alloys

V.Ya. DASHEVSKII et al.

Thermodynamic analysis of oxygen solutions in iron–nickel melts with chromium has been carried out. Since the bond strength of oxygen with such a melt becomes weaker with an increase in the nickel concentration ($\gamma^{\circ}_{O(Fe)}=0.0105$; $\gamma^{\circ}_{O(Ni)}=0.357$), the deoxidation power of the chromium in liquid nickel is higher than that in iron melt.

The deoxidation power of chromium remains almost constant when the nickel concentration in melt increases to 20% but it rises sharply with a further increase in its content. Oxygen solubility curves pass through a minimum, which shifts to lower chromium contents in a range of from −7% Cr (pure iron) to −1.7% Cr (pure nickel) when the nickel concentration rises. Minimum oxygen concentrations in nickel are lower almost by an order of magnitude as compared to iron. Subsequent chromium additions cause an increase in the oxygen concentration in melt; in this case, the higher the nickel content, the sharper the rise in the oxygen concentration after the minimum when chromium is added. Deoxidation of iron-nickel melts with chromium was experimentally studied for the Fe–20%Ni, Fe–40%Ni and Fe–60%Ni alloys. Experimental and calculated results are in good agreement.

(cf. *ISIJ Int.*, **45** (2005), 1783)

Lattice constant of iron and austenite including its supersaturation phase of carbon

I.SEKI et al.

Electrolytic iron powder was heated into γ-iron phase and carburized in austenite and its supersaturation phase under the gas mixture of CO and CO_2 with carbon activity of 0.1 to 1.0. The spacing of lattice planes of iron was measured using a high temperature X-ray diffractometry (XRD), which gradually increased with time and arrived at a constant value. The carbon concentration in samples after experiment was measured by a combustion-infrared absorptiometry. The lattice constants, a_0 (nm), of α-iron, γ-iron and austenite including its supersaturation phase of carbon have been determined as follows;

α-iron: $a_0=1.602\times10^{-9}T^2+2.059\times10^{-6}T+0.2860$ (295 to 1 183 K)

γ-iron: $a_0=8.1593\times10^{-6}T+0.35519$ (1 183 to 1 550 K)

Austenite: $a_0=0.35519+8.1593\times10^{-6}T+1.7341\times10^{-3}C$ (0 to 3.35 masss% and 1 452 to 1 550K)

where T and C are temperature (K) and carbon concentration (mass%), respectively.

(cf. *ISIJ Int.*, **45** (2005), 1789)

Prevention of resulfurization in desulfurization process with magnesium vapor produced *in situ* by aluminothermic reduction of magnesium oxide

J.YANG et al.

The mechanism of resulfurization in the desulfurization process with magnesium vapor produced *in situ* by aluminothermic reduction of magnesium oxide was clarified in the present work. The influences of various operating parameters on the resulfurization were studied and the methods that could prevent resulfurization were proposed.

There are two kinds of mechanisms of resulfurization in the desulfurization process with magnesium. One is decomposition of the desulfurization product of MgS under the inert atmosphere. The other is oxidation of MgS under the oxidative atmosphere.

Under the present experimental conditions, lowering operating temperature and oxygen partial pressure in the atmosphere, and adding more pellets containing magnesium oxide and aluminum could effectively prevent the resulfurization. The resufurization took place more markedly by using Al_2O_3 crucible than by using MgO or C crucible.

Adding CaO onto the melt surface was an effective method for preventing the resulfurization due to transformation of the desulfurization product of MgS into the more stable compound of CaS. For prevention of the resulfurization, using the CaO–Al_2O_3 mixture is less effective than using only CaO. Since addition of the activated charcoal powders greatly decreased the transfer rate of oxygen in the atmosphere to the melt surface, it also reduced the resulfurization remarkably.

(cf. *ISIJ Int.*, **45** (2005), 1795)

Chlorination and evaporation behaviors of $PbO–PbCl_2$ system in $Ar–Cl_2–O_2$ atmosphere

H.MATSUURA et al.

It is quite important to know the reactivity and behavior of Pb contained in steelmaking dust, or bottom ash and fly ash generated from municipal solid waste incineration process with chlorine. In the present study, chlorination and evaporation kinetics of $PbO–PbCl_2$ melt have been investigated in $Ar–Cl_2–O_2$ atmosphere from 1 023 to 1 123 K. The weight of PbO specimen increased first and then decreased in $Ar–Cl_2–O_2$ stream during experiments, which phenomena mean that produced $PbCl_2$ by PbO chlorination formed liquid oxychloride phase of $PbO–PbCl_2$ system and then $PbCl_2$ evaporated. Increase of partial pressure of chlorine increased the initial chlorination rate, however no effect on the latter evaporation rate was observed. Decrease of maximal weight gain of specimen and the slight increase of evaporation rate were observed with increasing partial pressure of oxygen. Activation energies of chlorination and evaporation of $PbO–PbCl_2$ melt in the steady state were 35 kJ/mol and 156 kJ/mol, respectively. Evaporation rate of $PbO–PbCl_2$ was also investigated at 1 073 K in $Ar–O_2$ atmosphere, however the change of evaporation rate with changing partial pressure of oxygen was within experimental error. Measured evaporation rate strongly depended on the composition of melt. Composition dependency of evaporation rate estimated from the activity of $PbCl_2$ for the $PbO–PbCl_2$ system generally represented the same trend, however the measured evaporation rate was larger than estimated one in the whole composition range. This result indicates that the formation of oxychloride melt affects the evaporation rate. Chlorination mechanisms and removal efficiency of Pb by chlorination have been discussed based on the present results.

(cf. *ISIJ Int.*, **45** (2005), 1804)

Vaporization behavior of zinc from the $FeO–CaO–SiO_2–Al_2O_3$ slag system

Y.ZHANG et al.

Vaporization behavior (1 000–1 300°C) of zinc in the slag system $FeO–CaO–SiO_2–Al_2O_3$ has been examined, including the formation ratio of vapor species and their partitioning, along with the effect of process factors such as temperature, duration time, slag composition, addition of reductive agents, and chlorine content. A thermodynamic estimation with the principle of Gibbs free energy minimization shows that the major vapor species from the sample of $FeO–CaO–SiO_2–Al_2O_3$ system+ZnO+$CaCl_2$ are metallic Zn, $ZnCl_2$ and $FeCl_2$ at the experimental temperature range. The results suggest that the formation ratio of metallic Zn and $FeCl_2$ increases, while that of $ZnCl_2$ decreases, with an increase in temperature. The evaporation of sample is initially fast and becomes steady after holding for 10 min. Gaseous $ZnCl_2$ is mainly formed during heating period, at the holding stage it reacts with FeO to produce gaseous $FeCl_2$. With regard to slag compositions, Fe^{2+}/Fe^{3+} ratio and basicity significantly affect the evaporation of zinc. The former governs the types of vapor species and the latter affects the total

volatile ratio of zinc. The evaporation ratio of zinc can be enhanced by the addition of reductants such as carbon powder. It also increases with the increasing ratio of $CaCl_2$/ZnO and levels off above 2.

(cf. *ISIJ Int.*, **45** (2005), 1813)

Ironmaking

Effect of coke micro-textural and coal petrographic properties on coke strength characteristics

R.SHARMA et al.

Coke texture is most important quality factor of blast furnace coke. A coke, as descends in blast furnace, it should retain essentially the same shape but is not true. In coke, its strength is associated with the micro-structure and texture. The carbonization of coals leads to the development of coke that exhibits a variety of microscopic textures whose optical behavior in polarized light aids in their characterization. The optical microscope provides the most appropriate method for measuring these features. In this study nine coke samples of different coal blend made by stamp charging technology (Wet Bulk density $1.15\,t\,m^{-3}$) were used and an attempt has been made to examine the microtexture of stamp charged coke in range of 23.4 to 24.6% volatile matter to predict coke strength by microtexture and possibilities of establishing vitrinite distribution-coke texture relationship, if any. Results indicate that cokes contain significant proportion of isotropic carbon and different size of anisotropic carbon. Anisotropic carbon is less reactive to carbon dioxide compared to isotropic carbon and the strength after reaction depends on its anisotropic texture. With an increase in isotropic carbon M10 index deteriorates and coke reactivity index increases. In this study it was also found that all the carbon forms mentioned do not correlate well with vitrinite distribution and hence, it can be stated that micro petrographic parameters are generally not sufficient for expressing decisive properties of coke; since, coke microstructure and texture has been recognized to be of prime importance in controlling and improving the physical properties of coke.

(cf. *ISIJ Int.*, **45** (2005), 1820)

Discrete particle simulation of solid flow in a model blast furnace

Z.ZHOU et al.

This paper reports a numerical study of solid flow in a model blast furnace under simplified conditions by means of discrete particle simulation (DPS). The applicability of the proposed DPS approach is validated from its good agreement with the experiment in terms of solid flow patterns. It is shown that the DPS is able to generate a stagnant zone without any need for any arbitrary treatment, and capture the main features of solid flow within the furnace at a microscopic level. The results confirm that the solid flow in a blast furnace can be divided into four different flow regions. However, the flow is strongly influenced by the front and rear walls in a 2D slot model furnace whereas the predicted stagnant zone decreases significantly with wall sliding friction. In a 3D model with periodic boundary conditions incorporated, a smaller stagnant zone is obtained. The effects of solid flow rate, particle properties such as sliding and rolling friction coefficients on the solid flow are also investigated. The results are analysed in terms of solid flow patterns, solid velocity field, porosity distribution and normal force structure. The implication to blast furnace operation is discussed.

(cf. *ISIJ Int.*, **45** (2005), 1828)

Steelmaking

A mathematical model to study liquid inclusion behavior at the steel-slag interface

J.STRANDH et al.

The separation of non-metallic inclusions at the interface between the steel and the slag in the ladle, tundish and mold is an essential part of the production of clean steel. It is therefore, of great importance to have a deep understanding of the phenomena controlling the transfer of inclusions from the steel to the slag layer. In this work a mathematical model, derived from the equation of particle motion, have been used to study the transfer of liquid inclusions to slags. The effects of the drag, added mass, buoyancy and rebound force on the inclusion transfer are considered. The model relies, to a great extent, on the availability of accurate information of the magnitude of a number of physical properties of the involved phases. Among those properties, the interfacial tension between the phases and the slag viscosity were found to be the most critical. Due to the fact that the availability of experimentally obtained high-temperature physical property data, relevant to the industrial conditions, is scarce in the literature several different model descriptions have been used in this work to estimate these properties. The mathematical model has been used to investigate the separation of liquid non-metallic inclusions, of different size and composition, to a number of different industrial ladle slag compositions.

(cf. *ISIJ Int.*, **45** (2005), 1838)

Numerical analysis on Si deoxidation of molten Fe, Ni, Fe–Ni, Fe–Cr, Fe–Cr–Ni, Ni–Cu and Ni–Co alloys by quadratic formalism

T.MIKI et al.

Numerical analysis on Si deoxidation of molten Fe, Ni, Fe–Ni, Fe–Cr, Fe–Cr–Ni, Ni–Cu and Ni–Co alloys have been carried out. The excess Gibbs free energy change of mixing has described with Redlich–Kister type polynomial using the relation derived from Darken's quadratic formalism. Excellent agreement between present work and experimental results was found for equilibrium Si and O contents in molten Fe, Ni, Fe–Ni, Fe–Cr, Fe–Cr–Ni, Ni–Cu and Ni–Co alloys. Si deoxidation equilibrium of not only one component metal but also alloys can be analyzed numerically using the formula determined in the present work. Also, interaction parameters of Redlich–Kister type polynomial can be easily converted into interaction coefficients with Taylor's series, which are widely used in steelmaking processes.

(cf. *ISIJ Int.*, **45** (2005), 1848)

Dissolution kinetics of alumina into mold fluxes for continuous steel casting

A.-H.BUI et al.

Dissolution kinetics of alumina into mold fluxes for the continuous steel casting was investigated by employing the rotating cylinder method. The dissolution rate of Al_2O_3 was determined by measuring weight loss of Al_2O_3 rod, initial dipping area and immersion time. It is concluded that the alumina dissolution is controlled not only by the mass transfer in the molten flux but also by the formation of intermediate compounds such as $CaO \cdot 6Al_2O_3$, $CaO \cdot 2Al_2O_3$, and $2CaO \cdot Al_2O_3 \cdot SiO_2$ on the rod/flux interface. Concentration driving force, rod rotation speed, temperature of molten flux and chemical composition are also important factors which affect the alumina dissolution. The dissolution rate increased with addition of MgO or CaF_2, or up to 5%mass of Na_2O, and then decreased with further increase in the amount of Na_2O content. The physical erosion of the rod surface by the solid $2CaO \cdot SiO_2$ dispersed in the liquid was attributed to fast alumina dissolution.

(cf. *ISIJ Int.*, **45** (2005), 1856)

Casting and Solidification

The observation of mold flux crystallization on radiative heat transfer

W.L.WANG et al.

As an important factor in the moderation of heat transfer in continuous casting mold, mold flux has been researched widely. However, the study of the effect of solid mold flux on radiative heat transfer has not been conducted widely. By using an infrared radiation emitter, which was developed at Carnegie Mellon University, a radiative heat flux was applied to a copper mold to simulate the heat transfer phenomena in continuous casting. The effect of adding a thin slag disc on top of copper mold on radiative heat transfer has been analyzed. It was found that the presence of mold flux enhanced radiative heat transfer rate. The effect of full crystallization of a slag disc was to reduce the heat transfer rate by 20% compared with a completely glassy sample. The specific effect of full crystalline and glassy parts of the mold flux on radiative heat transfer, and the influence of their properties on heat transfer rate was discussed in this paper.

(cf. *ISIJ Int.*, **45** (2005), 1864)

Chemical and Physical Analysis

Corrosion behavior in graphite refractories impregnated with ZrO_2 and CeO_2 carrying solutions

F.VERNILLI et al.

This paper investigates corrosion behavior in graphite refractory hot metal impregnated with ZrO_2 and CeO_2 carrying solutions used in Blast Furnace hearth, consisting of 50% graphite and 50% anthracite. Corrosions tests were carried out by means of finger test method in an induction furnace, using bar-shaped 30×30×280 mm test specimens and hot metal from CSN #2 Blast Furnace runner. The tem-

perature chosen for this test was 1 520°C and 60-min isotherm. Upon test completion, test specimens were characterized by their dimensional variation, X-ray diffractometry and Scanning Electronic Microscopy (SEM).

(cf. *ISIJ Int.*, **45** (2005), 1871)

Forming Processing and Thermomechanical Treatment

Influence of TiN particle precipitation state on static recrystallisation in structural steels

M.I.VEGA et al.

This paper studies the influence of different Ti and N contents, which give rise to different precipitation states at the reheating temperatures, on the static recrystallisation of austenite in structural steels. The influence of the precipitation state has been quantified by the changes in the activation energy value (Q_x), which measures the greater or lesser facility for grain boundary self-diffusion, the mechanism that is responsible for recrystallisation. A maximum has been obtained for the activation energy which corresponds to the finest precipitate distribution and a Ti/N ratio close to unity, although the excess Ti content in solution also contributes to a considerable increase in Q_x. The values obtained for the driving forces of recrystallisation have always been greater than the pinning forces, allowing static recrystallisation to take place irrespective of the chemical composition of the steel and the strain applied.

(cf. *ISIJ Int.*, **45** (2005), 1878)

Surface Treatment and Corrosion

Effects of carbon contents in steels on alloy layer growth during hot-dip aluminum coating

T.SASAKI et al.

Hot-dip aluminum coating of hypo-eutectoid steels containing 0.05–0.88 mass% carbon were performed, and the alloy layers formed in the coating were investigated. In the hot-dip aluminum coating at immersion temperatures ranging from 700 to 850°C, the alloy layers on the steels consisted of a single phase of the intermetallic compound Fe_2Al_5. The thickness of the alloy layer increased in proportion to the increasing square root of the immersion time ($t^{1/2}$) for immersion temperatures lower than 800°C for the whole base steel. On the other hand, for immersion temperatures higher than 800°C, the thickness of the alloy layer on the 0.05 mass% C steel and 0.45 mass% C steels exhibited a negative deviation from the linear relationship. The growth rate constant k decreased as the carbon concentration of the base steel increased up to 0.8 %, above which k had a constant value. The reaction activation energies for the base steel in this study were approximately 70–80 kJ/mol. The alloy layer/base steel interfaces were serrated, and the serration width decreased with increasing carbon concentration of the base steel. In addition, the serration width had a larger value in the immersion temperature range wherein the pro-eutectoid ferrite content in the base steel was larger.

(cf. *ISIJ Int.*, **45** (2005), 1887)

Transformations and Microstructures

Mapping the hot deformation microstructure of Ni–30Fe alloy

H.BELADI et al.

The evolution of structure during the hot working of an austenitic Ni–30%Fe alloy is studied using EBSD analysis of samples tested in torsion. A microstructural map in temperature–strain space that plots grain size, cell size, fracture and dynamic recrystallization is presented.

(cf. *ISIJ Int.*, **45** (2005), 1893)

Microstructural changes and crack initiation with white etching area formation under rolling/sliding contact in bearing steel

H.HARADA et al.

Microstructural changes during the formation of White Etching Area (WEA) were investigated using a rolling/sliding contact fatigue test machine. In particular, interfaces between WEA and retained austenite or spherodized carbide in a high carbon chromium bearing steel have been observed. Fatigue tests were carried out by means of a disk on roller-type equipment. It was found that acicular structures are formed at an initial stage of the WEA formation process. Plastic deformations of spherodized carbides were caused by shear stress in the initial stage of this process as well. Additionally, micro voids were found near the interfaces. Furthermore, amorphous-like structures were found in the WEA. It was suggested that WEA formation is caused by the local plastic deformation of the material. The shear stress was caused by slipping between the roller and the disk. As a result, it was suggested that martensite forms an amorphous-like phase and then changes into a WEA. Cracks developed in the amorphous-like structure/the granular area interface in the WEA and in the Matrix/WEA interface.

(cf. *ISIJ Int.*, **45** (2005), 1897)

An analysis of the transition between strain dependent and independent softening in austenite

M.R.CARTMILL et al.

The post-deformation softening behaviour of austenite has been studied for various compositions and deformation conditions. The strain at which the transition from strain dependent to strain independent post-deformation softening behaviour occurs (ε^*) has been found to coincide closely with the strain to the peak stress (ε_p) under certain conditions but not under others. It has been proposed that the relationship between ε^* and ε_p may be described geometrically using the initial grain size and the dynamically recrystallised grain size.

(cf. *ISIJ Int.*, **45** (2005), 1903)

Evaluation of the system free energy of the martensite phase in an Fe–Cr–C ternary alloy

T.KUNIEDA et al.

The system free energy was evaluated for the martensite phase of an Fe–Cr–C ternary alloy. The system free energy of the martensite phase is defined as, $G_{sys}=G_0+E_{str}+E_{surf}$, where G_0 is the chemical free energy, E_{surf} is the interfacial energy for the boundaries in the martensite microstructure, and E_{str} is the elastic strain energy due to the dislocations in the martensite phase. From the experimental results on SEM/EBSD, the interfacial energy was estimated to be 0.05 J/mol for the prior austenite boundary, 0.11 J/mol for the martensite packet boundary and 0.32 J/mol for both the martensite block and the lath boundaries in the as-quenched specimen. The total decrement in the interfacial energy accompanying annealing at 873 K for 100 h after quenching was estimated to be about 0.1 J/mol. Also, the elastic strain energy of the as-quenched specimen was evaluated to be 7.1 J/mol. The total microstructural energy of the martensite phase was about 10 J/mol, which operates as a driving force for the microstructure evolution, *e.g.*, recovery of dislocations and the coarsening of the sub-structures such as martensite-packet, -block and -lath.

(cf. *ISIJ Int.*, **45** (2005), 1909)

Mechanical Properties

High temperature creep flow and damage properties of the weakest area of 9Cr1Mo–NbV martensitic steel weldments

V.GAFFARD et al.

In the present study, creep flow and damage behaviour of modified P91 steel weldments are investigated. Premature creep failure of weldments (with respect to base metal) occurs in the intercritical heat affected zone (ICHAZ). This microstructure is reproduced by thermal simulation applied to blanks cut from the base metal. Metallurgical investigations of what happens during the welding cycle show that the weakest part of the heat affected zone is heated slightly below complete austenitisation, with little (if any) carbide dissolution. During the post-weld heat treatment, extensive recovery is allowed by carbide coarsening. The intrinsic creep behaviour of the resulting microstructure is experimentally determined under controlled constraint conditions. The welding cycle strongly decreases the creep strength by increasing the creep strain rate, but not necessarily by decreasing the ductility, at least for lifetimes up to 3 500 h.

(cf. *ISIJ Int.*, **45** (2005), 1915)

Study of the inelastic response of trip steels after plastic deformation

R.PÉREZ et al.

A study of the elastic response before and after tensile plastic strain was undertaken for two commercial low-alloyed TRIP steels. These steels, TRIP 700 (C–Mn–Al alloy) and TRIP 800 (C–Mn–Si) are commercial alloys used in sheet metal stamping. The behaviour of the instantaneous tangent modulus (E_T) *versus* stress during loading and unloading was measured for each degree of prestrain. Loading curves show a decrease in the E_T of the deformed samples as compared with the undeformed state. Though at low stresses a highly linear response was measured for both steels, a decrease was obtained for TRIP 700 as strain increased, whereas TRIP 800

remained unchanged. During unloading, a progressive decrease in E_T was obtained in all deformed states, with lower chord modulus values as the tensile plastic prestrain increased. The inelastic response observed is attributed mainly to microplastic strain caused by the displacement of mobile dislocations. Thus, the differences between the two TRIP steels studied are related to the microstructure and the different dislocation structures observed in them. A notable consequence of this study is a better accuracy in the prediction of springback passes due to a better understanding of these inelastic effects that stems from going beyond mere use of traditional Young's modulus values.

(cf. *ISIJ Int.*, **45** (2005), 1925)

Contribution of microstructural factors to hardness change during creep exposure in Mod.9Cr–1Mo steel

K.SAWADA et al.

The effect of microstructural factors on hardness was investigated in normalized, tempered, aged and crept materials for Mod.9Cr–1Mo steel, using nanoindentation and microhardness tests. Nanohardness and microhardness decreased during tempering, aging and creep exposure. Dislocation spacing, lath width, high angle boundary (block and packet boundary) spacing and inter-particle spacing increased during tempering, aging and creep exposure. A converted Vickers hardness was introduced to compare directly nanohardness and microhardness to Vickers hardness. The converted Vickers hardness increased with indent size in all the materials tested. Hardness at an indent size less than 1 μm mainly consists of dislocations inside lath grains. Hardness at an indent size larger than 1 μm originates from not only dislocation but precipitates and high angle boundaries such as block and packet boundaries. Comparing the converted Vickers hardness with lath width and high angle boundary spacing in normalized material with no precipitates, it was found that the lath boundary does not contribute to hardness. The difference in converted Vickers hardness between tempered and aged material was obviously large at the indent size, greater than inter-particle spacing. The decrease in hardness during aging is caused by increase in inter-particle spacing due to coarsening and coalescence of precipitates. On the other hand, not only changes in precipitates but also increase in high angle boundary spacing and dislocation spacing contribute to decrease in hardness during creep exposure.

(cf. *ISIJ Int.*, **45** (2005), 1934)