Fundamentals of High Temperature Processes

Kinetics of the non-isothermal reduction of Cr_2O_3 with aluminium

O.M.CINTHO et al.

The present paper presents the results of a thermoanalytical investigation on the kinetics of the aluminothermic reduction of Cr_2O_3 under non-isothermal conditions. Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) technique were used. It was determined the minimum molar ratio Cr_2O_3: Al for the completion of the reaction and the value of the change of enthalpy associated to the reduction. X-ray diffraction was used in order to identify the products of reduction. Since the oxidation of aluminium and the reduction of Cr_2O_3 occur simultaneously, it was possible to study the kinetics by analysing the rate of generation of the peak area for the Cr_2O_3 reduction (DTA) and the mass gain due to the oxidation of some of the excess of aluminium (TG). The reduction was controlled by first order chemical reaction and the reduction was isokinetic within the experimental conditions of the present work.

(cf. *ISIJ Int.*, **44** (2004), 781)

Investigation of *in-situ* chemical reactions of Al_2O_3-SiC-SiO_2-C refractory and its interactions with slag

L.HONG et al.

Experiments were carried out to investigate *in-situ* reactions of refractory and its interactions with slag (composition: 45.4%SiO_2+36.6%CaO+15.9%Al_2O_3) using a horizontal furnace by detecting CO and CO_2 contents in off gas with an infrared (IR) analyzer. The composition of refractory is 69.4%Al_2O_3+7.3%SiO_2+10.6%SiC+12.7%C. Temperature was from 1 773 to 1 873 K. The samples after high temperature experiments were analyzed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)—Energy Dispersive Spectrometer (EDS). Mullite was detected after refractory samples were maintained at high temperatures. The refractory/slag reaction was evaluated by calculating the carbon removed. Carbon removal process was a two-step reaction, in the beginning the carbon was removed very quickly (fast reaction stage) and both CO and CO_2 gases were detected by IR analyzer. Then after around 2 000 s the reaction slowed down and no CO_2 gas could be detected (slow reaction stage). The main *in-situ* reaction product was SiC rather than SiO. Slag showed good wetting with the refractory and penetrated into it through pores. Low melting point compounds, anorthite ($CaAl_2Si_2O_8$) and gehlenite ($Ca_2Al_2SiO_7$) were detected after heating refractory for 7 200 s while remaining in contact with slag.

(cf. *ISIJ Int.*, **44** (2004), 785)

Reduction behavior of EAF slags containing Cr_2O_3 using aluminum at 1 793 K

J.H.PARK et al.

The simultaneous reduction kinetics of Cr_2O_3, MnO, FeO, and SiO_2 in the EAF slag by aluminum has been investigated at 1 793 K to understand the reduction mechanism of each oxide in the stainless steelmaking conditions. The reduction degree of MnO reached about 90% and that of FeO and Cr_2O_3 reached about 80% for 5 min. The reduction degree of SiO_2 continuously increased up to about 55% for 20 min, followed by a constant value. The reduction of each oxide by aluminum was found to be controlled by the diffusional mass transfer process in slag phase from the simple kinetic analysis. The mass transfer coefficient of each oxide was in order of '$MnO > Cr_2O_3 \cong FeO \gg SiO_2$' in the present system. The reduction rate constant ($\log K_o^{MO}$, where MO represents Cr_2O_3, FeO, MnO, and SiO_2) linearly increases by increasing the product of diffusion coefficient and the activity of each oxide ($\log[D_M \cdot a_{MO}]$) in the slag.

(cf. *ISIJ Int.*, **44** (2004), 790)

Ironmaking

Computer simulation of heat transfer in regenerative chambers of self-preheating hot blast stoves

L.ZHONG et al.

Heat transfer in chambers of self-preheating hot blast stoves in Anshan Iron and Steel Co., China, has been numerically simulated with a three-dimensional unsteady heat conduction equation and an energy conservation equation for fluid flowing through channels in the chambers. The blast temperature and air preheating temperature in the numerical simulation study are in good agreement with those in measurement. The numerical results show that hot blast temperature can reach 1 200°C by using a self-preheating process and low calorific blast furnace gas under the studied operational conditions. Amount of heat exchange between the checkerwork and the fluids and usable heat increase in the middle and low parts of the chambers of the hot blast stoves due to the application of the self-preheating process.

(cf. *ISIJ Int.*, **44** (2004), 795)

Numerical analysis on injection of hydrogen bearing materials into blast furnace

M.CHU et al.

Injection of hydrogen bearing matters into blast furnace has been attracting technical and scientific interests aimed to improve the furnace performance through enhancing hydrogen reduction. In this study, the operations of humidified blasting, natural gas and waste plastics injections are numerically examined in comparison with all-coke operation by means of multi-fluid blast furnace model. The model evaluations are carried out under constant raceway conditions and hot metal temperature throughout all tested cases. Since the injection of hydrogen bearers changes raceway conditions, the blast conditions that are used for model computation as tuyere inlet boundary condition, including blast rate, oxygen enrichment, temperature and humidity, are suitably adjusted to maintain raceway temperature and bosh gas flow rate. The model simulations reveal that in-furnace temperature level lowers while the enhancement of hydrogen reduction reduces the ratio of direct reduction with hydrogen bearer injection. The productivity improves, and coke rate shows a little increase in humidified blasting operation while it obviously decreases in the injections of natural gas and waste plastics. The other two cases, namely, natural gas and waste plastics injections, show remarkable improvement of furnace efficiency. The decrease in heat demands by direct reduction, solution loss and silicon transfer reactions contributes to the improvement of blast furnace efficiency with respect to hydrogen bearer injection.

(cf. *ISIJ Int.*, **44** (2004), 801)

Steelmaking

The effect of bottom nozzle configuration on the bath behaviour in the BOF

M.J.LUOMALA et al.

The blowing behaviour of the BOF is affected in many ways by the behaviour of molten bath. Bottom blowing and its interaction with top blowing have a strong influence on splashing and spitting behaviour, bath homogenisation and bath oscillation. Therefore, three selected bottom nozzle configurations were studied by physical modelling, and the results were compared regarding splashing, homogenisation and oscillation of the bath. According to model tests, bottom nozzle positioning has a great influence on the amount and direction of splashing and spitting. Moreover, at lower lance gaps, the direction of splashes was changed because of bath oscillation. At low lance gap, when type A oscillation is dominant, correlation between the degree of overlap and stability of the bath was found. The bigger the degree of overlap, the more unstable the system as far as type A oscillation and splashing is concerned. The amplitude and oscillation frequency of the bath changed as a function of lance height. Blowing through bottom nozzles prevented the onset of so called type A oscillation. Bottom nozzle configuration of three nozzles resulted in shortest mixing time, lowest total splashing on model walls and longest starting time of type A oscillation.

(cf. *ISIJ Int.*, **44** (2004), 809)

Casting and Solidification

Combustion of carbon in casting powder in a temperature gradient

M.SUPRADIST et al.

The combustion of carbon in a packing of casting powder has been investigated in an apparatus simulating the thermal conditions in the continuous casting mold. The temperature gradient was established along the powder column and air was admitted at its cold upper surface. After the reaction time the column was cooled to room temperature and the carbon profile was determined. The results show a strong variation of carbon content along the column with the original content still existing at the top, a pronounced carbon minimum in the middle and a second minimum at the bottom. A mathematical model was developed for the theoretical investigation of the combustion problem. It involves the solution of the rate equations for the chemical reactions and of the differential equations for heat flow, transport of

gaseous species and continuity. The model produces carbon profiles in the packing and off-gas compositions which agree satisfactorily with those measured.

(cf. *ISIJ Int.*, **44** (2004), 817)

Influence of Na_2O on phase relation between mold flux composition and cuspidine

M.HANAO et al.

Phase relation between mold flux composition and cuspidine was researched fundamentally. Solidification temperatures of the mold flux were measured at various compositions, and crystal compositions in their solidified structure were identified by X-ray diffraction analysis. Based on these results, the phase relation between the mold flux composition and cupsidine was considered. In the relation between basicity ($T.CaO/SiO_2$) and the solidification temperature, there was a peak of the solidification temperature and the basicity at the peak varied according to the contents of Na_2O and F. Taking the affinity of F to Na rather than Ca into consideration, NaF was considered to exist as a component of the molten flux. Treating the mold flux composition as $CaO–SiO_2–CaF_2–NaF$ system, it became possible to estimate the phase relation between the mold flux composition and crystal composition such as cuspidine, CaF_2 and $NaCa_2FSiO_4$ accurately.

According to this study, conventional compositions of the mold flux were estimated to be out of the primary crystallization field of cuspidine. On the other hand, the composition of the mold flux, that enabled the high speed casting of hypoperitectic steel slabs at 5.0m/min without longitudinal surface cracking, was estimated to be in the field and close to be cuspidine.

(cf. *ISIJ Int.*, **44** (2004), 827)

Dissolution of ZrO_2, Al_2O_3, MgO and $MgAl_2O_4$ particles in a B_2O_3 containing commercial fluoride-free mould slag

A.B.FOX et al.

Non-metallic inclusions composed of ZrO_2, Al_2O_3, MgO and $MgAl_2O_4$ are associated with problems during the continuous casting of steels and so it is desirable that such particles dissolve completely if they appear in the slag. The dissolution behaviour of particles of these oxides in a fluorine-free slag containing 1.5 wt% B_2O_3, was studied *in situ* using Confocal Scanning Laser Microscopy (CSLM). The effects of particle type, initial size, and slag temperature were investigated. Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was performed to chemically analyze quenched samples, in order to identify any surface reaction or diffusion layers formed. Analytical prediction models were compared to the experimental data to relate the kinetics to possible rate-limiting steps. Thermodynamic solubility limits for use in the model were determined using commercial CALPHAD based software. The dissolution rates of Al_2O_3, MgO and $MgAl_2O_4$ were found to be comparable to one another whereas the dissolution rate of ZrO_2, is four times slower. The surface reaction appears to be controlling the rate of dissolution, with the activation energy for ZrO_2 being 128.8 kJ/mol and for $MgAl_2O_4$ being 77.8 kJ/mol. This implies that the removal of ZrO_2 particles by dissolution in this type of slag is not feasible for the typical residence times expected, and strategies that prevent the incorporation of these particles should be used.

(cf. *ISIJ Int.*, **44** (2004), 836)

Forming Processing and Thermomechanical Treatment

Kohonen network modelling for the strength of thermomechanically processed HSLA steel

S.DATTA et al.

Primarily from the point of view of improvement of yield strength due to additions of niobium, titanium and boron in HSLA steels, the experimental steels are divided into five classes. The data are then supplied for learning a Self Organising Map (Kohonen network). It is found that the network with six neurons possesses better capacity of prediction with unknown data. Another effort of clustering the steels according to its major strength contributing mechanisms is also made. But the capacity of the network to cluster unknown data is found to be rather poor and has failed to follow from the metallurgical principles. To avoid this limitation, Learning Vector Quantisation method is adopted to impart a certain amount of supervision in the learning process and it is found that the training pattern of the network attains a good convergence thereby leading to a good predictive ability.

(cf. *ISIJ Int.*, **44** (2004), 846)

Welding and Joining

Laser welding of 422 stainless steel with inconel 625 filler metal

T.C.YANG et al.

Laser welding of Type 422 stainless steel (SS) with Inconel 625 filler metal additions was investigated. Tensile, impact, and fatigue crack growth tests were performed on laser welds and 422 SS base plates as well. The soft zone, consisting of ferrite with extensive $M_{23}C_6$ carbides at grain boundaries, was observed in the heat-affected zone (HAZ) adjacent to the weld interface of 700°C/2 h tempered welds. The existence of soft zone in the weld was detrimental to impact toughness and caused brittle fracture at room temperature. Nevertheless, such a deteriorated effect was less severe at elevated temperatures. Either the soft zone or the weld metal (Inconel 625) did not affect the strength of welds in tensile tests. Consequently, the fracture location of laser-welded specimens was in the base metal at both 25 and 540°C. The fatigue crack growth rates (da/dN) in the weld metal and HAZ of the weld after tempering were less than those of the 422 SS base material for similar ΔK ranges. The retardation in da/dN was obvious at low ΔKs for the weld tempered at 700°C/2 h. Such retardation became very significant and an accelerated da/dN in the HAZ was resulted if the tempering treatment was not performed on the weld.

(cf. *ISIJ Int.*, **44** (2004), 852)

Surface Treatment and Corrosion

High nitrogen stainless steel as a preferred substratum for bacteria and other microfouling organisms

K.R.SREEKUMARI et al.

High Nitrogen steels (HNS) have gained importance in recent years as construction materials. Their resistance to pitting corrosion makes them better candidates for industrial use. In the medical field, these materials are welcomed as their use can minimize the risk of nickel allergy. Nitrifying bacteria are a group of bacteria widely distributed in soils, freshwater, seawater *etc.* and since they derive their energy by oxidation of nitrogen compounds, they pose a threat to these materials. Experiments on the adhesion of nitrifying bacteria on HNS were carried out following coupon exposure method in the laboratory. *Nitrobacter winogradskyi* (nitrite oxidizing bacteria) and *Nitrosomonas europea* (ammonia oxidizing bacteria) were used for the adhesion studies. In addition, adhesion of a heterotrophic strain, *Pseudomonas* sp. also was studied for comparison. Materials used for the experiment were AISI type 304 L, 304 LN, and high nitrogen stainless steels. The results showed that *Nitrobacter winogradskyi*, *Nitrosomonas europea* and *Pseudomonas* sp., invariably, adhered more on the high nitrogen stainless steel coupons compared to the other two types of coupons tested. During the initial stages, *i.e.* on the first day, the trend was not so clear, but as the exposure period increased the pattern has clearly evolved. The area of adhesion showed a gradual decrease going from HNS, to 304 L through 304 LN coupons. The acidic metabolic products of nitrifying bacteria might interact with the surface of HNS, disturbing the equilibrium of ammonium ion formation, thereby leading to localized corrosion. Exposure to a natural freshwater pond showed a heavy microfouling load on HNS coupons. The consequences of preferential adhesion of bacteria and other microfouling organisms on the corrosion resistance of HNS are discussed. As a possible means to mitigate bacterial adhesion on HNS, silver contained high nitrogen stainless steel was tested. The results suggested a significant decrease in bacterial adhesion on silver containing HNS compared to 304 L and HNS.

(cf. *ISIJ Int.*, **44** (2004), 858)

The use of river clam shells (aspatharia sinuata) as an energizer in case carburization of mild steels

D.U.I.OGO et al.

River clam shells (aspotharia sinuata) which mainly contains calcium carbonate ($CaCO_3$) was explored for use as an energizer during pack-carbonization process. The mild steel samples were pack-carbonized at 950°C for various time duration in carbonizing compounds containing a mixture of charcoal and varying amounts of clam shells up to a maximum of 50% clam shell ($CaCO_3$) as energizer. Some other samples from the same stock were also pack carbonized using 100% charcoal. The carbonization depths of the heat treated samples were

measured using a micro hardness tester. The results showed that river clam shell is an effective energizer with maximum hardness obtained with the composition of 70% charcoal +30% river clam shells.

(cf. *ISIJ Int.*, **44** (2004), 865)

Transformations and Microstructures

Influence of the geometry of an immersed steel workpiece on mass transfer coefficient in a chemical heat treatment fluidised bed

W.GAO et al.

The mass transfer during carburising in a fluidised bed and in a steel workpiece has been studied experimentally in this work. This involved carburising experiment in an electrically heated fluidised bed at 900–970°C with natural gas and air as the atmosphere. A steel workpiece was designed to provide a range of carbon transfer surfaces of different geometries in the fluidised bed, and the carbon transfer coefficient was measured at these surfaces. The carbon transfer coefficient was determined from the carbon distribution within the diffusion layer of the sample. An empirical relationship of the carbon potential as a function of carburising atmosphere, bed temperature and fluidising velocity was determined, based on the understanding of the mass transfer mechanism and analysis of the experimental results.

(cf. *ISIJ Int.*, **44** (2004), 869)

Microstructure evolution mechanism in iron aluminides/CrMo steel composite prepared by solid state bonding

N.MASAHASHI et al.

This work addresses a mechanism of columnar microstructure evolution during diffusion bonding in a composite of iron aluminide and CrMo steel focusing on the role of alloying on microstructure. Columnar microstructure develops in the steel side of diffusion couples of iron aluminide and Fe–X (X=Cr, Mo) steel, when the steel composition is in the gamma phase at the bonding temperature. This is consistent with the proposed model for columnar microstructure evolution, which contributes to bonding strength between iron aluminide and steel. Interdiffusion coefficient at the Matano interface decreases with increasing the concentration of alloying elements in steel, and its decrease rate is higher for Mo than for Cr. The columnar grains in the steel side of the couple are longer than expected by chemical composition analysis, and their lengths increase with the interdiffusion coefficient. Microstructure evolution mechanism is discussed in terms of the kinetics of nucleation and subsequent grain growth during diffusion bonding.

(cf. *ISIJ Int.*, **44** (2004), 878)

Differential scanning calorimetry and microscopy study of transformations in ductile cast irons: part I. continuous heating

R.IVANOVA et al.

The kinetics of pearlite to austenite and ferrite to austenite transformations in two ductile cast irons are studied using differential scanning calorimetry, optical microscopy, electron microprobe, X-ray diffraction and microhardness techniques. Study of the heating process up to the austenitic range with ferrite–pearlite metal base showed presence of a set of phase transformations taking place in different temperature intervals. These transformations are the Curie transformation, pearlite to austenite transformation, and ferrite to austenite transformation. The change of the heating rate influences in different degrees the shift of the temperature ranges where the different phase transformations take place, depending on the type of transformations, and therefore alters significantly the time–temperature parameters of the phase transformations. It has been found that the peak temperatures of the Curie transformation at heating rates 1 and 50°C/min are 739 and 745°C (for the Fe–3.38C–3.23Si–0.33Mn alloy) and 739 and 746°C (for the Fe–3.75C–2.91Si–0.39Mn alloy), respectively. The increase of the temperatures with the heating rates is more significant for pearlite to austenite and ferrite to austenite transformations. The peak temperature of the ferrite to austenite phase transformation at heating rates 1 and 50°C/min are 837 and 876°C for the Fe–3.38C–3.23Si–0.33Mn alloy and 823 and 853°C for the Fe–3.75C–2.91Si–0.39Mn alloy, respectively. The observed micro-inhomogeneity of the silicon influences significantly the kinetics of the phase transformations. The thermal effect due to the Curie point (T_c) is detected, and the influence of the continuous heating parameters on the Curie transformation is studied.

(cf. *ISIJ Int.*, **44** (2004), 886)

Differential scanning calorimetry and microscopy study of transformations in ductile cast irons: Part II. continuous cooling

R.IVANOVA et al.

The study of the cooling processes of ductile cast irons using the differential scanning calorimetry technique in the temperature range of 20–950°C shows three thermal effects. They are due to three transformations: the restoration of magnetic properties (T_{Cc}), austenite→pearlite transformation (T_{Pc}), and austenite to ferrite plus graphite transformation (T_{Fc}). The data allow studying the kinetics of the transformations at different testing conditions, cast iron composition and as-cast microstructure. During cooling the temperature sequence at which the transformations occur is $T_{Fc}>T_{Cc}>T_{Pc}$. The increase in cooling rate changes the intensity and temperatures of the different transformations in different ways. This results in the overlapping of the thermal effects.

(cf. *ISIJ Int.*, **44** (2004), 896)

Effect of microstructure on the cold headability of a medium carbon steel

X.MA et al.

Cold headability is the ability of a cylindrical metallic specimen to be shaped at high strain rate into the head of a bolt, screw or other cold-formed part without cracking. This property is material dependent and can be influenced by many factors such as chemical composition, surface condition, and microstructure. The effect of microstructure upon the cold headability of a medium carbon steel (1036M) was investigated. Six different microstructures were produced by various heat treatments. Drop weight tower (DWT) testing methods, previously developed at McGill University, were used on samples of these materials. Visual inspection, metallographic and SEM analysis were carried out to detect cracks on the surfaces of tested samples and to identify their causes. The axial and circumferential strains of the tested samples were measured and the strains at which cracks were initiated were used to assess the headability. The cold headability was found to be particularly sensitive to the microstructure and was greatest in the completely spheroidized structures. This indicates that DWT testing is a valid method for evaluating the cold headability of metallic materials.

(cf. *ISIJ Int.*, **44** (2004), 905)

Mechanical Properties

Deformation behaviors around/at the interface between Zn-electrodeposition and Fe-substrate

K.NAKAI et al.

In order to examine the deformation behaviors at/around the interface between η-Zn electrodeposited layer and α-Fe substrate with Burgers orientation relationship, $(110)_{Fe}//(0001)_{Zn}$ and $[\bar{1}11]_{Fe}//[11\bar{2}0]_{Zn}$, slip systems operated at/around the interface have been analyzed using X-ray back-reflection Laue method, optical microscope and stereographic analyses. The Zn-electrodeposited specimen was deformed at room temperature under a tensile strain rate of 2.8×10^{-3}/s. Under low tensile strains below 10%, slip systems having large Schmid factor operate in Fe-substrate. In Zn-layer, slip systems having smaller Schmid factor operate to relax the tensile strain at the interface due to deformation in Fe-substrate, suggesting the constraint due to the cohesion at the Zn/Fe interface. As increasing the tensile strain, the slip systems forming corrugated configuration operate in Fe-substrate and their shear strains at the interface are difficult to be relaxed smoothly by deformation of Zn-layer. As increasing tensile strain, twinning occurs in Zn-layer and the slip system with low critical resolved shear stress operates in the twinned region. The decohesion of Zn-layer from Fe-substrate is induced as increasing the twinned region in Zn-layer.

(cf. *ISIJ Int.*, **44** (2004), 914)

Life prediction of low alloy ferritic steels based upon the tertiary creep behavior

S.FUJIBAYASHI et al.

In the present work, the applicability of the Θ projection to the life prediction for 1.25Cr–0.5Mo and 2.25Cr–1Mo steel has been examined. The linear relationship between strain rate and strain at the tertiary creep stage is observable and its slope, which is equivalent to Θ_4 in the Θ projection technique, can be uniquely correlated with rupture life independently of chemical compositions, creep strength and testing conditions. Therefore, it can be considered that strain rate monitoring for the rem-

nant life prediction is very effective to improve the accuracy of the life assessment, especially for parent material of a low alloy ferritic steel in which creep cavitation is rather unlikely.

(cf. *ISIJ Int.*, **44** (2004), 919)

Physical Properties

Effect of manganese partitioning on transformation induced plasticity characteristics in microalloyed dual phase steels

N.R.Bandyopadhyay et al.

The manganese contents of the dual phase steels with transformation induced plasticity characteristics are reasonably high. Efforts have been made to study the role of manganese in making stable austenite. The effect of the varying holding time at different intercritical annealing temperatures on the formation of manganese enriched austenite by a competitive process have been studied. The effect of manganese partitioned austenite so produced on the TRIP behaviour of the steel has also been studied through processing structure property correlation. It is seen that manganese enrichment in retained austenite depends on the time and temperature of intercritical annealing.

(cf. *ISIJ Int.*, **44** (2004), 927)

Social and Environmental Engineering

Elution mechanism of fluorine from steelmaking slag into seawater

T.Miki et al.

Steelmaking slag contains nutrition such as Si, P and Fe and it is reported by our group that dissolved Si, P, Fe can accelerate phytoplankton growth by photosynthesis. Phytoplankton can fixate more carbon dioxide at unit earth surface area than any other creature on this planet. This means that by educing the potential of steelmaking slag, suppression of CO_2 in the atmosphere and utilization of steelmaking slag can be achieved.

In consideration of nutrition supply from steelmaking slag to seawater, we must avoid hazardous element dissolution from steelmaking slag into seawater. The elution mechanism of fluorine into the artificial seawater has been studied based on dissolution behavior of fluorine from synthesized fluorine containing substances into artificial seawater in the present work.

(cf. *ISIJ Int.*, **44** (2004), 935)