

Fundamentals of High Temperature Processes

Occurrence and composition of some mineral phases in the tuyere coke

S GORNOSTAYEV *et al*

Polished sections of tuyere coke were studied by optical and scanning electron microscopy and wavelength-dispersive analysis (WDS) to reveal structural and chemical changes occurring with mineral phases (K- and Na-, \pm Ca-bearing aluminosilicates). The aluminosilicates in the tuyere coke form new compounds, which occur as particles with smooth outlines (spherules and irregular segregations), which are of larger size than their parental particles. The depth of the diffusion zone between particles of the parental mineral phases and new phases was found to be 5–20 μm , and it reflects a trend towards reducing free surface energy. It was determined that total K+Na drops from the parental particles to the new phases. Relative enrichment of K over Na (increase of K/Na_{m} ratio) was traced from the parental mineral phases towards the final agglomerated phase, which may indicate an Na excess in the circulating gases and/or the carbon phase of the coke. On the other hand, the K/Na_{m} ratio decreases during formation of spherules that point to loss of K. Micrometers-range WDS profiles across the spherules revealed variable alkali behavior, with some spherules characterized by a strong negative correlation of alkalis, indicating ordering of the alkali cations and the existence of K–Na substitution. The alkali total (K+Na) and balance (K/Na) changes observed during this study suggest that at least one point of alkali escape begins upon the release of these elements during the formation of spherules and irregular segregations of K- and Na \pm Ca-bearing aluminosilicates.

(cf *ISIJ Int*, 45 (2005), 1)

Deoxidation equilibrium of aluminum and silicon in the liquid iron–nickel alloys

VYDASHEVSKII *et al*

Thermodynamic analysis and experiments showed the deoxidation ability of aluminum in the iron–nickel melts to be lower than that in pure iron and nickel. With an increase in the nickel content, the deoxidation ability of aluminum decreases to about 50% Ni and then it rises. In pure nickel, the deoxidation ability of aluminum is almost equal to that in pure iron. On one hand, this can be explained by an increase in the bond strength of aluminum with this melt when the nickel content rises ($\gamma_{\text{Al(Fe)}}^{\circ} = 0.049$, $\gamma_{\text{Al(Ni)}}^{\circ} = 0.00022$) and, on the other hand, by a decrease in that of oxygen ($\gamma_{\text{O(Fe)}}^{\circ} = 0.0105$, $\gamma_{\text{O(Ni)}}^{\circ} = 0.357$). Curves of the oxygen solubility pass through the minimum whose location is independent of the nickel content in melt. The minimum oxygen concentrations are reached at $\sim 0.2\%$ Al, the further additions of aluminum result in a rise in the oxygen concentration. Experimental and calculated results are in good agreement.

Complex deoxidation of Fe–40%Ni with aluminum and silicon has been experimentally studied. The formation of solutions and chemical compounds between oxides of these elements promotes the participation of silicon in the deoxidation. The

lower oxygen concentrations are reached after the combined deoxidation in comparison with the aluminum deoxidation. However, when the aluminum content rises in the melt at the same silicon concentration, this difference decreases, at a certain aluminum concentration, its deoxidation power becomes equal to that of complex action of aluminum and silicon. This occurs due to an increase in the content of aluminum oxide in slag. When the slag is saturated with aluminum oxide ($a_{\text{Al}_2\text{O}_3} = 1$), silicon does not take part in the deoxidation.

(cf *ISIJ Int*, 45 (2005), 8)The effect of Na_2O and Al_2O_3 on dephosphorization of molten steel by high basicity MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slagG Li *et al*

Highly basic CaO based slags saturated with MgO have been studied with respect to the phosphate capacity by measuring the phosphorous distribution ratio between slag and metal under controlled oxygen partial pressure at 1823 K and 1873 K. The effect of Na_2O and Al_2O_3 addition and the activity of FeO and $\text{FeO}_{1.5}$ were also determined. The phosphate capacity for MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ slag containing 0 to 5 mass% Al_2O_3 and 0 to 1.75 mass% Na_2O at 1873 K are in the range of $10^{18.37}$ to $10^{19.00}$ and that containing 4.1 to 5.0 mass% Al_2O_3 and 0 to 2.37 mass% Na_2O at 1823 K are in the range of $10^{18.53}$ to $10^{18.62}$. For the slags containing 21.28 to 23.59 mass% Al_2O_3 and 0 to 4.25 mass% Na_2O at 1823 K are in the range of $10^{17.84}$ to $10^{18.15}$.

The addition of Na_2O to the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system increases the phosphate capacity of the slags. Alumina in the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system decreases the phosphate capacity of the slags. The addition of Na_2O to the MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system decreases the activity coefficients of FeO and $\text{FeO}_{1.5}$ and those of P_2O_5 . The activity coefficients of FeO and $\text{FeO}_{1.5}$ show that they all behave as an acidic oxide in MgO saturated $\text{CaO-FeO}_x\text{-SiO}_2$ system.

(cf *ISIJ Int*, 45 (2005), 12)Kinetics of the non-isothermal reduction of Nb_2O_5 with aluminiumC PD LAZZARI *et al*

The present paper presents the results of a thermoanalytical investigation on the kinetics of the aluminothermic reduction of Nb_2O_5 under non-isothermal conditions. Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) technique were used. It was determined the minimum molar ratio $\text{Nb}_2\text{O}_5/\text{Al}$ 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 Nb_2O_5 occur simultaneously, it was possible to study the kinetics by analysing the rate of generation of the peak area for the Nb_2O_5 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 con-

ditions of the present work

(cf *ISIJ Int*, 45 (2005), 19)

Thermodynamics of titanium and nitrogen in Fe–Si melt

J–J PAK *et al*

The thermodynamics of titanium and TiN formation in Fe–Si–Ti–N melts was studied. A metal–nitride–gas equilibration technique was used to measure the activities of titanium and nitrogen in the presence of pure solid TiN under various nitrogen pressures in the temperature range of 1843–1923 K. The activity coefficients of titanium and nitrogen relative to 1 mass% standard state in liquid iron were calculated from the experimental results for Fe–Si alloys of silicon content up to 2.26 mass%. The first- and second order interaction parameters of silicon on titanium, $e_{\text{Ti}}^{\text{Si}}$ and $r_{\text{Ti}}^{\text{Si}}$, were determined as -0.0256 and 0 at 1873 K, respectively. Similarly, the interaction parameters of silicon on nitrogen, e_{N}^{Si} and r_{N}^{Si} , were determined as 0.0491 and 0 at 1873 K, respectively. The temperature dependence of these interaction parameters was also determined. The validity of thermodynamic parameters determined in the present study was examined by observing the formation of TiN precipitates in a Fe–1%Si–Ti–N melt of controlled titanium and nitrogen contents at 1873 K.

(cf *ISIJ Int*, 45 (2005), 23)

Casting and Solidification

Vortexing flow patterns in a water model of slab continuous casting mold

B Li *et al*

A water model experiment was conducted to observe the vortexing flow in the steel slab continuous casting mold, the snake-shaped Plexiglas mold was designed to simulate the actual caster. The camera was used to record the flow patterns, which were visualized by injecting the black sesames into water. The changes of shape of single vortex and two vortices with time have been observed during experiments. A numerical model has been developed to analyze the vortexing flow, which may be produced by moving the submerged entry nozzle from center to off-center in the slab continuous casting of steel. According to the numerical results, the vortexing flow is resulted from three-dimensional biased flow in the mold. A vortex is located at the low velocity side adjacent to the submerged entry nozzle. The vortex strength depends on the local horizontal velocity of fluid and decreases gradually with distance from the free surface. The vortexing zone size depends on the biased distance of the submerged entry nozzle, and intensity of the vortexing flow depends on the casting speed of the continuous caster.

(cf *ISIJ Int*, 45 (2005), 30)

A new equiaxed solidification predictor from a model of columnar growth

D J BROWNE

A new indicator of the potential for the formation of an equiaxed zone during alloy solidification is

proposed. The indicator, or equiaxed index, is calculated from the predictions of a numerical model of non-equilibrium columnar solidification. This model uses a front-tracking approach to simulate the nucleation and growth of an undercooled columnar dendritic front into the liquid phase in a 2D casting process. The algorithm for the advancing front is based on expressions developed from considerations of dendrite tip growth. A comparison is made with models in which growth of individual, and competing, columnar crystals are simulated. The equiaxed index is based on numerical integration of an undercooled ravine in front of the advancing columnar front, and changes with time. This proposed metric is a predictor of the relative tendency to form an equiaxed zone. Study of the peak values confirm that equiaxed solidification is more likely in concentrated alloys, and also where the rate of heat extraction to the mould is low. This is in agreement with experimental data from the literature.

(cf *ISIJ Int.*, **45** (2005), 37)

Forming Processing and Thermomechanical Treatment

Mathematical modeling of draft schedule for inline rolling of ultra thin strip in the combined single-belt casting/hot rolling process

S ZHOU *et al*

The single-belt process is a new route to produce steel strips, in which the single-belt caster is directly connected with hot mills. This process should be able to roll strip with thickness 1 mm or below. In hot rolling of the ultra thin strip there are many limitations which are represented by the finishing rolling temperature of the strip, the oxidation of the strip, the overheat of the roll and the maximum rolling speed. In the present paper the possibility of hot rolling ultra thin strip in the single-belt process was investigated. On the basis of mechanical/thermal/metallurgical behavior of the strip a mathematical model of draft schedule was proposed. In terms of different criteria the draft schedule was optimized. The results show that austenitic hot rolling of ultra thin strip in the single-belt process can be carried out like the conventional hot rolling for low carbon steels. With consideration of roll life the maximal roll surface temperature has a large influence on the establishment of the draft schedule for hot rolling of ultra thin strips.

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

Examination of oxide scales of hot rolled steel products

R Y CHEN *et al*

Porosities in the scale layer and wavy scale-steel interfaces are two common artefacts generated during metallographic preparation of oxide scale samples. This paper presents the techniques used by the authors to effectively remove porosities in the scale and reduce the waviness of the scale-steel interface so that the true scale structures can be examined. The techniques have been successfully applied to the examination of oxide scales on hot-rolled steel with various thicknesses and

structures

(cf *ISIJ Int.*, **45** (2005), 52)

Welding and Joining

CO₂ laser welding characteristics of 800 MPa class TRIP steel

T-K HAN *et al*

Basic characteristics of CO₂ laser welded 800 MPa class TRIP steel such as defects, microstructure, mechanical properties and formability was investigated. Bead-on-plate welding was carried out under various power, welding speed and shield gas. Porosity fraction reduced with increasing the welding speed and using Ar-He mixed shield gas compared to Ar gas. The maximum hardness was obtained at the weld metal as well as HAZ near the weld metal. The value was the same regardless of welding speed and was nearly equal to that of water quenched raw metal. In the perpendicular tensile test to the weld axis, the joints produced at optimum condition were fractured at the base metal and the tensile property was nearly equal to the raw metal. In a parallel tensile test, the strength of the joints was higher than that of the base metal, but elongation was found to be lower than that of the raw metal because a crack was initiated in the bead at the strength levels corresponding to the tensile strength of the base metal and was propagated perpendicular to tensile direction. Elongation and formability were further improved using low power or Ar+He mixed gas compared to high power or Ar gas.

(cf *ISIJ Int.*, **45** (2005), 60)

Influence of welding parameters and shielding gas composition on GTA weld shape

S LU *et al*

The interaction between the variable welding parameters and shielding gas composition in determining the weld shape in Ar-CO₂ shielded gas tungsten arc (GTA) welding with SUS304 stainless steel is discussed. The GTA weld shape depends to a large extent on the pattern and strength of the Marangoni convection on the pool surface, which is controlled by the content of surface active element, oxygen, in the weld pool and the welding parameters. Results showed that oxygen absorption into the liquid pool during the welding process is sensitive to the CO₂ concentration in the shielding gas. An inward Marangoni convection occurs on the pool surface when the oxygen content is over 100 ppm in the welding pool under Ar-0.3%CO₂ shielding. A low oxygen content in weld pool changes the inward Marangoni convection to an outward direction under the Ar-0.1%CO₂ shielding. The strength of the Marangoni convection on the liquid pool is a product of the temperature coefficient of the surface tension ($d\sigma/dT$) and the temperature gradient (dT/dr) on the pool surface. Different welding parameters will change the temperature distribution and gradient on the pool surface, and therefore, affect the strength of Marangoni convection and the weld shape.

(cf *ISIJ Int.*, **45** (2005), 66)

Surface Treatment and Corrosion

Analysis of the initial stage of localized corrosion on Zn and Zn alloy coated steels by photon rupture method

M SAKAIRI *et al*

A photon rupture method, film removal by a focused pulse of pulsed Nd-YAG laser beam irradiation, has been developed as it enables oxide film stripping at extremely high rates without contamination from the film removal tools. In the present study, Zn and Zn-5mass%Al alloy coated steel specimens covered with protective nitrocellulose film were irradiated with a focused pulse of a pulsed Nd-YAG laser beam at a constant potential in 0.5 kmol m⁻³ H₃BO₃-0.05 kmol m⁻³ Na₂B₄O₇ (pH=7.4) with/without 0.05 kmol m⁻³ of chloride ions to investigate the initial stage of localized corrosion. At low potentials, both samples reformed oxide film after the nitrocellulose films were removed by this method. The oxide film formation kinetics of Zn-55mass%Al follow an inverse logarithmic law, in agreement with Cabrera-Mott theory. However, at high potentials, localized corrosion producing corrosion products occurred at the area where nitrocellulose film was removed. The dissolution current of the Zn coated steel samples is higher than that of Zn-5mass%Al coated samples at the same applied potential.

(cf *ISIJ Int.*, **45** (2005), 71)

Inhibition of conversion process from Fe(OH)₃ to β-FeOOH and α-Fe₂O₃ by the addition of silicate ions

S-K KWON *et al*

To examine the influence of silicate ions on a conversion process of condensed ferric hydroxide Fe(OH)₃ gel to ferric oxyhydroxides and iron oxides, the Fe(OH)₃ gel was aged at 60°C in the presence and absence of silicate ions. Fine particles and supernatant solution were sampled from the aged suspensions containing colloidal particles. Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been used for characterizing the resulting solid particles. XRD profiles and TEM micrographs showed that the Fe(OH)₃ gel transferred into β-FeOOH and α-Fe₂O₃ particles by aging in the absence of silicate ions. On the other hand, silicate ions suppressed the conversion of the Fe(OH)₃ gel to β-FeOOH and α-Fe₂O₃ particles. The conversion of the Fe(OH)₃ gel to α-Fe₂O₃ particles is almost independent of pH of solution under the conditions in the present study, indicating that silicate ions essentially suppress the formation of β-FeOOH and α-Fe₂O₃ particles.

(cf *ISIJ Int.*, **45** (2005), 77)

Transformations and Microstructures

Modelling of microstructure evolution during hot rolling of a 780 MPa high strength steel

N NAKATA *et al*

The microstructure evolution during thermo-mechanical processing of a state-of-the-art Ti-Nb

HSLA steel with a tensile strength of 780 MPa has been investigated with laboratory investigations. The entire hot strip rolling process was simulated with hot torsion tests. Using the Gleeble 1500 thermomechanical simulator, constitutive behaviour, static recrystallization and austenite decomposition were quantified with single and double hit tests as well as continuous cooling transformation (CCT) tests. Precipitation strengthening was studied using aging tests. Based on the experimental results a microstructure model is proposed for hot rolling, run-out table cooling and coiling of the investigated steel. The model has been applied to predict the microstructure of industrially processed coils. The prediction of the ferrite grain size is seen to be in good agreement with that obtained during industrial hot strip rolling.

(cf *ISIJ Int*, 45 (2005), 82)

Effect of austenite grain size on the morphology and crystallography of lath martensite in low carbon steels

S MORITO et al

The crystallography, microstructure and mechanical property of as-quenched martensite of Fe-0.2C-Mn(-V) alloys of which the prior austenite grain sizes are 370–2 μm were studied. The prior austenite grain, whose size is larger than 28 μm , is divided by several packets. Those packets are subdivided by blocks containing sub-blocks, each of which corresponds to the Kurdjumov-Sachs variant. When the prior austenite grain size is about 2 μm , one packet tends to grow predominantly. Each packet is divided by blocks containing sub-blocks.

(cf *ISIJ Int*, 45 (2005), 91)

Effect of nitriding on grain oriented silicon steel bearing aluminum

T KUMANO et al

All high permeability GO is manufactured using AlN as the main inhibitor. Two types of inhibitor preparation of GO have been realized industrially, i.e., extra high and extra low slab reheating temperature methods. Therefore, from a purely metallurgical viewpoint, the possibility of a middle temperature slab reheating method was examined and the effect of nitriding was investigated.

Metallurgically, this method is located between the Extra high and Extra low temperature methods. Furthermore, it is essential that a suitable combination of inhibitor intensity and primary diameter, controlled by nitriding and heat treatments respectively can provide sharp Goss orientation.

(cf *ISIJ Int*, 45 (2005), 95)

Dependence of solvus temperature of the laves phase on (Mo+W+Re) contents in high Cr ferritic steels

Y MURATA et al

The solvus temperatures of the Laves phase were investigated in heat resistant 10Cr ferritic steels containing 2.3–4.7 mass% (Mo+W) and 0–1.7 mass% Re. The measured solvus data was approximately represented as a solvus curve in the pseudo-binary

system of Fe-W (+Mo). The solvus temperatures increased with increasing content of Mo+W in the steels, for example, 1020 K for 2.3 mass% (Mo+W) steel, 1130 K for 3.7 mass% (Mo+W) and 1145 K for 4.7 mass% (Mo+W) steel. It was suggested from the measured solvus curve that the Laves phase precipitated at 923 K granularly in a 2 mass% W steel, but finely in a 4.5 mass% W steel. On the other hand, the solvus temperature did not change with the Re addition up to 1.7 mass%.

(cf *ISIJ Int*, 45 (2005), 101)

Phase equilibrium between austenite and MX carbonitride in a 9Cr-1Mo-V-Nb steel

M YOSHINO et al

Precipitation behavior during normalizing heat treatment has been investigated on a 9Cr-1Mo-V-Nb steel. Heterogeneously distributed spherical MX (M=Nb, V, Cr and X=C, N) carbonitride particles and platelet M_3C (M=Fe, Cr) carbide were observed in the as normalized condition. Number of the precipitates decreased with increasing normalizing temperature and no precipitates was observed after normalizing at 1250°C. Although the size of M_3C was almost constant independent of normalizing temperature, that of MX increased with increase in normalizing temperature up to 1200°C. For MX carbonitride, not only size, but also composition of metallic elements was influenced by normalizing temperature. Since equilibrium composition of MX carbonitride depends on temperature, MX particle with non-equilibrium composition dissolves and precipitation of it takes place with its equilibrium composition at the normalizing temperature. A phase field diagram of NbX-VX quasi binary system in a 9Cr-1Mo-V-Nb steel was experimentally determined. It has been supposed that precipitation of M_3C takes place during cooling from normalizing temperature in the surrounding area of MX particles where the concentration of niobium and vanadium in matrix is poor.

(cf *ISIJ Int*, 45 (2005), 107)

Difference in the role of non-quench aging on mechanical properties between acicular ferrite and ferrite-pearlite pipeline steels

M-C ZHAO et al

Hot-rolled plates of both acicular ferrite (AF) and ferrite-pearlite (FP) pipeline steels were reheated at approximately 600°C, named as non-quench aging. In this paper the experimental result indicated that the non-quench aging caused different effects in mechanical properties for different microstructural types of pipeline steels. AF pipeline steels could be greatly strengthened by non-quench aging while FP pipeline steels could not be. Role of non-quench aging on mechanical properties between AF and FP pipeline steels was analyzed. Strengthening for AF pipeline steels by a subsequent simple non-quench aging without any other change in chemical composition, TMCP and rolling equipment, etc., provides a lower economical cost approach for the development of high strength pipeline steels.

(cf *ISIJ Int*, 45 (2005), 116)

Mechanical Properties

Certainty factor estimation using petri neural net for HSLA steel

S DATTA et al

An unsupervised learning technique and an associative memory have been used for encoding weights by a special type of Petri network named Petri neural net for modelling the influence of alloying elements on the final property of the high strength low alloy steel. The combined effects of alloying elements for different strengthening mechanisms is predicted when weights and threshold values are chosen on the basis of metallurgical understanding. The technique is found to be effective to create an associative memory of input-output relations in unknown data sets so that the same can be subsequently be used as a predictive tool.

(cf *ISIJ Int*, 45 (2005), 121)

Fatigue crack initiation in an interstitial free steel

N NARASIAH et al

The initiation of small cracks has been studied on dumb-bell-shaped plate type specimens of an interstitial free (IF) steel at the load ratio of $R=0$ under varied cyclic stress amplitudes between 0.6 and 1.0 of yield stress. Nucleation of cracks were observed at ferrite-ferrite grain boundary (FFGB) as well as inside ferrite grain body (FGB), but the former location was found to be the preferred one. The average length of FFGB cracks is found larger than that of the FGB cracks for identical cyclic loading conditions. The formation of slip bands inside the grain body, slip band impingement at grain boundary and elastic-plastic incompatibility synergistically influence the event of crack initiation in the investigated steel. In addition, nucleation of voids inside slip bands was found to be a new phenomenon associated with the above possibilities to affect the nucleation of cracks in the investigated steel.

(cf *ISIJ Int*, 45 (2005), 127)

New Materials and Processes

The effects of the oxygen-enriched surface layer on mechanical properties of $\alpha+\beta$ type titanium alloys

H FUKAI et al

The effects of heat treating conditions on thickness of the oxygen-enriched layer or α -case in Ti-4.5%Al-3%V-2%Fe-2%Mo alloy were studied in comparison with Ti-6%Al-4%V alloy, and then the effects of these layers on the mechanical properties were investigated. The higher heating temperature and an extended heating time increased oxygen-enriched layer or α -case thickness in Ti-4.5%Al-3%V-2%Fe-2%Mo alloy, and atmospheric heating using high purity argon gas with 99.999% purity could not prevent formation of the oxygen-enriched layer even by heating at such a low temperature as 998 K. The 30 μm thick oxygen-enriched layer without α -case was formed by heat treating at 1048 K for 3.6 ks in use of 99.9% purity argon gas which corresponded to the typical heating

conditions adopted in a practical superplastic forming (SPF) operation using Ti-4.5%Al-3%V-2%Fe-2%Mo alloy. The thickness of both surface layers in Ti-6%Al-4%V alloy was much thicker than Ti-4.5%Al-3%V-2%Fe-2%Mo alloy because of its higher heating temperature. Tensile elongation, fatigue strength and bendability were deteriorated with the increase of oxygen-enriched layer or α -

case thickness, and removal of these layers by pickling treatment fully recovered these properties to an original level. Deterioration of the mechanical properties was exerted by existence of the surface layer with high hardness, and in particular, the oxygen-enriched layer with α -case decreased fatigue strength more pronouncedly compared with the surface layer without α -case. Existence of brittle sur-

face layer with high hardness and the coarse grain size in α -case appeared to be responsible for accelerated formation of microcrack at the surface of the mechanical testing specimens, resulting in deterioration of various properties.

(cf. *ISIJ Int.*, **45** (2005), 133)