（＊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

Carburization of iron by Ar–CO–H_2 at 1 523 K

R.ASANO et al.

The rate of carburization of iron in Ar–50%CO–10%H_2 gas mixture at 1 523 K have been gravimetrically investigated. It is found that the Ar–CO–H_2 system carburizes faster than Ar–CO, because H_2 combines faster with adsorbed oxygen than does CO. Based on the established results of H_2O and CO_2 dissociation rate, the rate constant (k_3) of the recombination reaction of H_2 and adsorbed oxygen (O_{ad}) is calculated. It was found that k_3 is about 37.5 times larger than that (k_1) of CO and O_{ad}, while the measured k_3 in the present study is only 2.5 times larger than k_1. With the increase of carbon content, the corresponding equilibrium pH_2O* at the reacting surface of Fe–C melt becomes sufficiently small. Accordingly the produced H_2O easily reaches to the equilibrium pressure of pH_2O* due to the very fast recombination reaction of the H_2 and Oad. This is the reason that the addition of H_2 has small contribution to the overall carburization reaction after liquid phase is formed. Take into account the effect of the produced H_2O, rate of carburization (v) in CO–H_2 atmospheres is given by the equation: $v = k_1 pCO\theta_0 + k_3 pH_2\theta_0(1 - pH_2O/pH_2O^*)$, where θ_0 is the fractional coverage by adsorbed oxygen, pH_2O is the partial pressure of formed H_2O at the interface.

(cf. *ISIJ Int.*, **42** (2002), 121)

Carbide capacity of CaO–Al_2O_3–CaF_2 slag at 1 773 K

J.H.PARK et al.

The influence of CaF_2 on the thermodynamic behavior of carbon in the CaO–Al_2O_3–CaF_2 slag at 1 773 K was investigated on the basis of carbide capacity concept. The carbide capacity increases with increasing CaF_2 content up to about 25 mol%, followed by nearly constant value in the CaO_{satd}–Al_2O_3–CaF_2 system. The capacity in the CaO–Al_2O_3–CaF_2 (44–49 mol% CaO) system rapidly increases by increasing the $X_{CaF_2}/X_{Al_2O_3}$ ratio up to about unity, and then the capacity-increasing rate decreases at $X_{CaF_2}/X_{Al_2O_3} \geq 1$. The carbide capacity increases with an increase of CaO/Al_2O_3 ratio at a fixed CaF_2 content; also, the addition of CaF_2 greater than about 14 mol% would have no effect on capacity regardless of CaO/Al_2O_3 ratio. The iso-carbide capacities obtained in the present work are very similar to the iso-sulfide capacities available in the literature.

(cf. *ISIJ Int.*, **42** (2002), 127)

Leaching behavior of fluorine-containing minerals in seawater

H.HE et al.

The leaching behavior of F-containing hot metal dephosphorization slags (HM-slag) in seawater has been found different from that in distilled water. F-containing slags demonstrate higher dissolution degree in seawater, and the F content is lower in the case of seawater due to the precipitation of F-containing $Mg(OH)_2$ which favorably occurs at solid/seawater interface where pH is higher than 10. This F-bearing $Mg(OH)_2$ is not a stable form of F-containing mineral in seawater. It follows from the present study that, of the F-containing minerals in the HM-slags observed, only CaF_2 and $Ca_5(PO_4)_3F$ are stable in marine environments. The F solubility of CaF_2 is independent of pH, while that of $Ca_5(PO_4)_3F$ increases with increasing pH. The F content in seawater saturated with CaF_2 and $Ca_5(PO_4)_3F$ is all below 10 ppm regardless of pH.

(cf. *ISIJ Int.*, **42** (2002), 132)

Immobilization of hexavalent chromium in aqueous solution through the formation of 3CaO·$(Al,Fe)_2O_3$·$Ca(OH)_2$·xH_2O phase, ettringite and C–S–H gel

H.HE et al.

The immobilization of hexavalent chromium in aqueous solution is found to occur through the formation of Cr^{6+}-bearing AFm phase, ettringite and C–S–H gel, which are formed by calcium aluminate or ferrite, a mixture of lime and $Al_2(SO_4)_3$ or $Fe_2(SO_4)_3$, and calcium silicate, respectively. In the case of AFm phase, which is most effective one to the immobilization of Cr^{6+}, the Cr^{6+} concentration in aqueous solution decreases from initial 50 ppm to below 0.05 ppm. The Cr^{6+}-containing AFm phases identified are $3CaO \cdot Al_2O_3 \cdot Ca[(OH)_2,CrO_4] \cdot 18H_2O$, $3CaO \cdot (Al,Fe)_2O_3 \cdot Ca[(OH)_2,CrO_4] \cdot 18H_2O$, $3CaO \cdot Fe_2O_3 \cdot Ca(CO_3,CrO_4) \cdot 12H_2O$ and $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$. The immobilization occurs through the OH^- or CO_3^{2-} site substitution with CrO_4^{2-}. No significant amount of Cr^{6+} is identified in either ettringite phase or C–S–H gel, indicating that these two phases do not play an important role for the immobilization of Cr^{6+} in cement-based solidification/stabilization process. The immobilization takes place by the substitution of SO_4^{2-} site in the case of ettringite, while in the case of C–S–H gel the sorption mechanism is more possible.

(cf. *ISIJ Int.*, **42** (2002), 139)

Deoxidation equilibrium of Cr–Ni stainless steel with Si at the temperatures from 1 823 to 1 923 K

K.SUZUKI et al.

In order to clarify the effects of Ni and Cr on the Si deoxidation of liquid Fe–Cr–Ni alloy, the deoxidation equilibria of Fe–Ni and Fe–Cr–Ni alloys with Si were studied. The experiments were conducted on the conditions up to 20 mass% Ni in the Fe–Ni system and up to 18 mass% Cr and 9 mass% Ni in the Fe–Cr–Ni system at the temperatures of 1 823, 1 873 and 1 923 K. Results obtained were summarized as follows:

The effect of Ni on the interaction coefficient of Si was expressed by

$$\log f_{Si}^{Ni} = -0.009[\%Ni] + 2\times10^{-4}[\%Ni]^2,$$
$$[\text{mass\%Ni}] \leq 20, \quad 1\,823 \leq T \leq 1\,923\ \text{K}$$

The cross product terms concerning Cr and Ni on the interaction coefficients of Si and O dissolved in Fe–Cr–Ni alloy were expressed by

$$r_{Si}^{(Cr,Ni)} + 2r_O^{(Cr,Ni)} = -0.001, \quad 1\,823 \leq T \leq 1\,923\ \text{K}$$

The deoxidation product $K'_{Si} = [\%Si] \cdot [\%O]^2$ was numerically expressed by

$$\log K'_{Si} = 8.40 - 24\,600/T - (1.40 - 3\,500/T)[\%O] + 0.029[\%Si] - (0.047 - 246/T + 4.3\times10^{-4}[\%Cr])[\%Cr] - (0.003 + 2\times10 - 4[\%Ni])[\%Ni] + 0.001[\%Cr][\%Ni]$$

$$[\text{mass\%Cr}] \leq 25, \quad [\text{mass\%Ni}] \leq 20, \quad 1\,823 \leq T \leq 1\,923\ \text{K}$$

(cf. *ISIJ Int.*, **42** (2002), 146)

Ironmaking

Lattice parameter and redox equilibria in CaO-containing wustite

T.INAMI et al.

Equilibrium relation among oxygen potential in atmosphere, composition and lattice parameter in CaO-containing wustite have been studied at 1 273 K. Wustite plates with the molar cation fraction $M_{Ca}/(M_{Fe}+M_{Ca})$ ($=M_{Ca-Fe}$) ranging from 0.0058 to 0.079 were equilibrated with CO–CO_2 gas mixtures. Composition of the wustite specimens was determined by chemical analysis and thermo-gravimetric method. Lattice parameter of the CaO-containing wustite was measured by X-ray diffraction method. The relation between the lattice parameter $\boldsymbol{a}$ and the gas ratio Ks ($=P_{CO_2}/P_{CO}$) in the gas mixture was expressed by

$$\boldsymbol{a} = (4.2975 + 0.560 \cdot M_{Ca-Fe}) - 1.470\times10^{-2} \cdot \ln(Ks) \quad (\text{Å})$$

The variation of $\boldsymbol{a}$ with M_{Ca-Fe} and molar ratio M_{Fe}/M_O in the CaO-containing wustite was given by

$$\boldsymbol{a} = 1.916 + 0.565 \cdot (M_{Ca-Fe}) + 4.719 \cdot (M_{Fe}/M_O) - 2.316 \cdot (M_{Fe}/M_O)^2 \quad (\text{Å})$$

Then the lattice parameter may be used as the index of the composition in CaO- containing wustite. The 'iso-lattice-parameter' line was drawn within the wustite field in the isothermal section of the system FeO–Fe_2O_3–CaO. The molar ratio $M_{Fe_2O_3}/M_{FeO}$ of the CaO-containing wustite on the Fe_2O_3-rich side slightly increases with an increase in CaO content but the ratio on the FeO-rich side does not change. The solubility of CaO in the wustite equilibrated with both metallic iron and $2CaO \cdot Fe_2O_3$ was estimated to be ~9 mol% CaO.

(cf. *ISIJ Int.*, **42** (2002), 150)

Steelmaking

The effect of addition of Al_2O_3 on the viscosity of CaO–"FeO"–SiO_2–CaF_2 slags

F.SHAHBAZIAN et al.

The viscosities of CaO–"FeO"–SiO_2–CaF_2 slags with various amounts of alumina addition were measured using a rotating-cylinder method in the temperature range 1 714–1 757 K. The first part of the experiments was conducted by measuring the viscosities under equilibrium conditions after small additions of Al_2O_3. Similar experiments were also conducted with one commercial mould flux in order to compare the results. In both cases, the viscosities were found to increase with the addition of Al_2O_3 at

all the experimental temperatures, the increase in viscosity being somewhat linear with Al_2O_3 addition. In the case of the commercial mould flux, even an addition of 2.6 mass% Al_2O_3 led to a significant increase in the viscosity.

Some isothermal experiments were also conducted with the above set of slags in the dynamic mode, wherein, the changes in the slag viscosities were monitored as a function of time as an Al_2O_3 disc dissolved continuously into the slag. The experiments were so designed that the dissolution of alumina occurred mainly along the vertical direction. The rate of dissolution of alumina is discussed in the light of the rate of change of viscosity as well as the composition profile in the slag after the experiments. An examination of the Al_2O_3 disc revealed the counter diffusion of the slag components into the solid alumina and that the dissolution took place by the solid product dissolving in the melt.

(cf. *ISIJ Int.*, **42** (2002), 155)

Casting and Solidification

Development of a three dimensional mathematical model of the electromagnetic casting of steel

R.KAGEYAMA et al.

The development of a mathematical model for the electromagnetic casting of steel is described. The model is three dimensional and computes the evolution of the electromagnetic field, the turbulent liquid metal flow and the free surface of the metal pool with time. This is achieved by simultaneous solution of the MHD form of Maxwell's equations, Ohm's law, the Navier–Stokes and continuity equations (by large eddy simulation) and an equation for the free surface. Solution is by a combination of finite element (field and flow equations) and finite difference (surface equation) methods on an Eulerian-Lagrangian grid. The model was first tested against measurements, by others, of magnetic fields and induced currents in an apparatus akin to an electromagnetic caster, and then against computations, performed using finite difference methods by other investigators, of laminar flow within a 2D rectangular cavity. The model was also tested against classical equations for the oscillations of a free surface in a rectangular trough and then against measurements, at Nippon Steel Corporation, of the surface oscillations of a mercury pool surrounded by an inductor carrying alternating current. Use of the model to predict the behavior of a steel caster is to be described in a subsequent paper.

(cf. *ISIJ Int.*, **42** (2002), 163)

Continuous casting of billet with high frequency electromagnetic field

H.KIM et al.

In order to develop the high frequency electromagnetic continuous casting technology for applying to steel, numerical analysis of the magnetic field and casting experiments using various parameters have been conducted. The method of using cold inserts was well established to lead to a reliable numerical model. According to this numerical model, it was predicted that while casting, the magnetic field would be concentrated on the common region occupied by the coil and the melt and further its maximum value would be seen just below the melt level. Casting experiments have been carried out using tin as a simulating material for steel. No oscillation mark was observed on the billets because the solidification started without hook. Under an optimum condition, billet surface roughness was improved to 1/10 of the conventionally cast billets. The surface quality of the billet was heavily dependent on the melt level, the casting speed, and the coil current. In case of the excessive coil current, wave marks other than the oscillation mark appeared on the billet surface. The billet with proper electromagnetic conditions showed a thinner solid shell at the early stage of the solidification and a thicker shell at the mold bottom in comparison with the conventional cast billet. It has been concluded that the Joule heat is a more dominant factor than the magnetic pressure in determining the surface quality of cast products in the high frequency electromagnetic continuous casting process.

(cf. *ISIJ Int.*, **42** (2002), 171)

Welding and Joining

The effect of dilution on HAZ liquation cracking in PTAW Ni-base superalloys overlay deposit

B.HYUN et al.

In this study, the effects of dilution on the HAZ liquation cracking susceptibility of PTAW (Plasma Transferred Arc Welding) Inconel 625 and Inconel 718 overlay on Nimonic 80A were observed. In order to evaluate the HAZ liquation cracking susceptibility, the Varestraint test was utilized. A possible mechanism of HAZ liquation cracking was suggested, on the basis of microstructure examination and thermal analysis.

The HAZ liquation cracking of the diluted Inconel 625 and Inconel 718 with Nimonic 80A was closely related with solidification temperature range and the amount and distribution of γ/NbC and γ/Laves eutectic phases formed along the solidification grain boundaries. As the dilution was increased, the C/Nb ratio increased, while the amount of eutectic phases decreased. The solidification temperature range was lowered with increases in the dilution in each overlay. Therefore susceptibility of HAZ liquation cracking diminished with increases in dilution.

(cf. *ISIJ Int.*, **42** (2002), 178)

Transformations and Microstructures

Martensitic transformation and shape memory effect in ausaged Fe–Ni–Si alloys

Y.HIMURO et al.

Martensitic transformations in the Fe–(24–30)Ni–(5–8)Si (mass%) alloys have been investigated by means of optical and transmission electron microscopy, differential scanning calorimetry and hardness-testing. The Ms temperature is decreased by Si addition and the morphology of martensite is mainly lenticular in the unaged specimens. However, a pronounced decrease in the Ms temperature and a change in the martensite morphology from the lenticular to the thin plate type are observed on ausaging at 400°C. The increase in austenite hardness, the decrease in the Ms temperature and the increase in the tetragonality of martensite after ausaging at 400°C are clarified as due to the formation of nanoscale particles of γ'-$(Ni,Fe)_3Si$ with the $L1_2$ structure during ausaging at 400°C. The Fe–Ni–Si alloys that form thin plate martensite show the shape memory effect, which arises from the reverse transformation of stress-induced martensite to austenite. Precipitation hardening of the austenite phase by fine γ' particles during ausaging improves the degree of shape recovery.

(cf. *ISIJ Int.*, **42** (2002), 184)

Mechanical Properties

Effect of β phase stability at room temperature on mechanical properties in β-rich $\alpha+\beta$ type Ti–4.5Al–3V–2Mo–2Fe alloy

GUNAWARMAN et al.

The stability of the β phase at room temperature in various microstructures of a β-rich $\alpha+\beta$ type Ti–4.5Al–3V–2Mo–2Fe alloy and its relationship with the fracture toughness, hardness and tensile properties were investigated. A variety of microstructures were established by varying solution treatment temperatures in $\alpha+\beta$ field, cooling rate after solution treatment and the condition of subsequent second-step annealing treatment after air-cooling treatment. These microstructures have β phase with lattice parameters of β phase ranging between 0.3244 nm and 0.3221 nm. The stability of β phase, which is indicated by decreasing lattice parameter of β phase, is increased by either lowering cooling rate or formation of diffusional transformation products (secondary phases) in the β phase. The β phase with lattice parameter of β phase around 0.3242 nm is the minimal instability of unstable β phase at room temperature for attaining deformation-induced martensite in tensile specimens. There exists a proper degree of β phase stability for increasing the fracture toughness, J_{IC}. The relatively higher fracture toughness is obtained at low or high stability of β phase. The high fracture toughness at low stability of β phase (unstable β) is mainly due to the deformation-induced martensite. While, the high fracture toughness at high stability of β phase (stable β) is mainly due to the secondary phase in the β phase that produces a prominent crack deflection toughening mechanism. However, the relatively lower fracture toughness is obtained at high stability of β phase when the β phase contains small amount or no secondary phase. This leads to conclude that, if only the β phase stability is taken into account for explaining fracture mechanism, the fracture toughness would decrease monotonously with increasing stability of β phase. The Vickers hardness is nearly independent of stability of β phase.

(cf. *ISIJ Int.*, **42** (2002), 191)

A constitutive model for transformation superplasticity under external stress during phase transformation of steels

H.NAM et al.

Most models of superplastic deformation behavior under external stress during phase transformation have been derived under the assumption of plastic deformation in the weaker phase. In the present paper, we suggested a constitutive model for the transformation induced superplastic deformation of steels based on a concept of MIgration of Transformation Interface induced Plasticity (MITIP) including the phase transformation kinetics. The concept is that the migration of atoms in the transformation interface is a principal mechanism of superplastic deformation under stresses during phase transformation. The model could well describe the effect of the cooling rate, the transformed phase and the transformation temperature on the amount of the transformation induced superplastic strain. In order to calculate the deformation behavior under stresses during phase transformation of steels, the elastic strain, the volumetric strain due to thermal and phase transformation, the viscoplastic strain, and the transformation induced superplastic strain were taken into account. The calculated results were found to be in good agreement with the experimental data obtained from literature.

(cf. *ISIJ Int.*, **42** (2002), 200)

Physical Properties

Intergranular and internal oxidation during hot rolling process in ultra-low carbon steel

T.KIZU et al.

Intergranular and internal oxidation in slab reheating process for hot-rolling was investigated for ultra-low carbon steel with 0.01 mass% Si. Intergranular oxidation depth significantly increased at 1 473 K because of melting of Fe–Si–O complex oxides and decreased with increasing oxidation temperature at above 1 473 K. The depth increased with increasing oxidation time in the range of 1 800–5 400 sec and decreasing partial pressure of oxygen in the range of 1–10%. The maximum interval between intergranular oxidation was 210 μm, while austenite grain size observed at high temperature by a confocal laser microscope was over 1 mm. The size of "quasi-austenite" grains considered sites of ferrite grains was consistent with this interval. Internal oxides were formed underneath the scale and around the intergranular oxides. The thickness of internal oxidation layer extending beyond the furthest point of permeation by intergranular oxide increased with increasing oxidation temperature, time and with decreasing partial pressure of oxygen. The oxidation loss of substrate increased with increasing oxidation temperature, time and partial pressure of oxygen. The intergranular oxidation depth and the thickness of internal oxidation layer can be theoretically calculated by using oxidation loss rate of substrate and oxygen diffusion rate in austenite.

(cf. *ISIJ Int.*, **42** (2002), 206)

Social and Environmental Engineering

Development of PCM for recovering high temperature waste heat and utilization for producing hydrogen by reforming reaction of methane

N.MARUOKA et al.

For efficient heat-recovery of high temperature waste gas such as LDG in the form of latent heat, the utilization technology of phase change material, PCM, was experimentally studied. Copper balls as the PCM were encapsulated by nickel film with/without an insertion of carbon or ruthenium as an inhibition layer, based on an electro-plating method. Then, the effect of the film thickness on the strength of capsules was experimentally examined. As a result, the obtained PCM had enough strength by increasing the film thickness and showed an excellent catalytic property for reforming reaction from methane to hydrogen. In conclusion, the copper PCM with the thick film of nickel and an inactive layer between nickel and copper was available for producing hydrogen by recovering high-temperature waste heat efficiently.

(cf. *ISIJ Int.*, **42** (2002), 215)