Fundamentals of High Temperature Processes

Simultaneous decarburization and denitrogenization of molten iron with vacuum suction degassing method

M.AHMADI et al.

A kinetic study has been made on simultaneous decarburization and denitrogenization of molten iron in low content ranges by using Vacuum Suction Degassing method (VSD method). A porous Al_2O_3-SiO_2 tube was immersed into molten iron. Internal pressure of the tube was reduced to remove gaseous products from the tube-molten iron interface. The initial carbon and nitrogen contents were in the ranges of 0~1 000 ppm and 50~100 ppm, respectively. The initial oxygen content was below 50 ppm. The atmosphere of the bath surface was Ar (1.01×10^5Pa). The experimental temperature was 1 853 K.

The VSD method can greatly increase the rate of denitrogenization as well as decarburization, and the carbon and nitrogen contents can be decreased to very low values. The decarburization rate constant increases with increasing gas permeability of the porous tube and with decreasing its internal pressure. The decarburization at higher carbon content is largely affected by the dissociation reaction of solid oxide of the tube. The decarburization enhances the denitrogenization considerably. The denitrogenization reaction rate is strongly dependent on gas permeability of the porous tube. A mixed control model is applied to explain the denitrogenization at the porous tube-melt interface. It is found that the denitrogenization rate is controlled by the mass transfer in the porous tube wall at lower permeability and mainly by the chemical reaction at the tube-melt interface at higher permeability.

Reduction of iron oxide in sulfur bearing slag by graphite

L.HONG et al.

The effect of sulfur on the reduction rate of iron oxide in slags by graphite was investigated under argon atmosphere at 1 573 K. The slag basicity ($=(N_{CaO}+N_{Li_2O})/(N_{SiO_2}+N_{Al_2O_3})$); N : mol fraction) was varied between 1 and 2. The sulfur concentration controlled by addition of CaS or FeS to the primary slag was changed from 0.0045 to 4.45 mass%. The initial iron content was varied between 3.89 and 9.33 mass%, and the rotation speed of graphite rod ranged from 0 to 15 s^{-1}.

It is found that the rate of iron oxide reduction decreases by the sulfur addition. In a slag, 20.5% Li_2O-38.4% CaO-41.1% SiO_2, when the sulfur content is less than 1.33%, the reduction rate decreases with the increase in sulfur content, but above 1.33% it hardly changes. Under the condition of gas hold-up factor in the foam-

ing slag, $\varepsilon = 0.4$, the reduction rate dose not change with the condition of graphite rod rotation, but increases a little under the foam-free condition.

The effect of sulfur on the reduction of iron oxide becomes larger with decreasing silica activity. It is considered that under the present experimental conditions, the reduction of iron oxide in the slags is mainly controlled by chemical reaction affected by interfacial adsorption of sulfur and silica.

Effects of oxygen and nitrogen on the rate of nitrogen dissolution in iron-chromium and iron-vanadium alloys

H.ONO et al.

The rate constant of nitrogen dissolution in a Fe-20mass%Cr has been measured as a function of oxygen content by ^{14}N-^{15}N isotope exchange reaction at 1 973 K. Adsorption coefficient of oxygen on a Fe-20mass%Cr at 1 973 K has been determined to be 100 in terms of [mass%] from present results. This value is smaller than that on pure iron (0 mass%Cr), 144, which was determined by our previous work. Moreover, dependence of the rate constant of nitrogen dissolution in Fe-Cr and Fe-V alloys on nitrogen partial pressure has been measured by the same technique in order to investigate the adsorption effect of nitrogen itself. Adsorption coefficient of nitrogen calculated from present results is much smaller than that of oxygen and it is confirmed that nitrogen is not so surface active as oxygen in molten Fe-Cr and Fe-V alloys. However, it is observed that the value of adsorption coefficient increases from 0.0509 to 0.156 in terms of $\sqrt{P_{N_2}}$ by addition of chromium up to 60 mass% Cr at 1 873 K. Addition of vanadium is more effective for increasing the adsorption coefficient and the value for Fe-6.2mass%V at 1 973 K is 6 times larger than that for pure iron.

Ironmaking and Reduction

Increase of pulverized coal use efficiency in blast furnace

A.BABICH et al.

Replacement of metallurgical coke by pulverized coal (PC) injected in blast furnace (BF) tuyeres is a major economical challenge, due to the high price of coke and unfavorable effect of its production for the environment. But the difficulty consists in necessity of complete gasification of coal particles within raceway and compensating for the negative changes in technology.

Theoretical and experimental researches of PC burning process under conditions of raceway have been carried out. Methods and designs for intensifying burning have been developed. Among them there are enriching blast with oxygen and its rational use, apply-

ing physical methods and chemical additives. Laboratory and industrial tests of these methods have shown the possibility of considerable raise of PC combustion degree under high PC consumption.

Effect of coal composition on its use efficiency in BF operation have been examined. Technical and economical parameters of BF operation when injecting PC from different coals have been calculated. Recommendations to coal grinding and method of complex compensating for the changes in technological regime have been developed.

Steelmaking and Refining

Electronic states of oxygen irons of molten slags used for iron and steel making

M.MORISHITA et al.

Regarding molten slags used for iron and steel making, discrete anion models, SiO_4^{4-} and $Si_2O_7^{6-}$, coordinating metal ions such as Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} were examined by the DV-Xα method. The bond order which is a measure of the covalent bond and the ionicity which is a measure of the charge transfer were calculated. The bond orders between the Si ions and the uni-bonding oxygen ions were found to be very high. On the other hand, the bond orders between the Si ions and the oxygen ions coordinating the metal ions were very low, that is, the covalent bonds between them are weak, indicating that these oxygen ions appear to become free oxygen ions. The metal ions such as Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} are necessary for the formation of the free oxygen ions as well as the decomposition of polymerized structures. The values of ionicity of the uni-bonding oxygen ions were -0.5~-1.2 and those of the oxygen ions coordinating the metal ions were -2.3~-2.5. These values of oxygen ions are approximately equal to the valences obtained from the statistical thermodynamics studies.

Casting and Solidification

Influence of carbon content on the growth angle of steel dendrites in a flowing melt

H.ESAKA et al.

Using both experiments and numerical analysis, the influence of carbon content on deflection angle of dendrites has been studied. Experimental studies have been carried out using wide range of carbon contents. Numerical analysis has relied on finite-volume computer simulations. With the help of these techniques, it has been observed that the deflection angle increases with increasing carbon content. Dimensions of dendrite (dendrite tip radius and primary dendrite arm spacing) play

Analysis and Characterization

Chromium and nitrogen segregation in thin oxide layers formed on the surface 17Cr-Ni-Mo-N austenitic steels studied by angle resolved XPS

S.Suzuki et al.

Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) has been used for characterizing thin oxide layers formed on the surface of 17Cr-Ni-Mo-N austenitic steels. It was confirmed that chromium and nitrogen segregation takes place on the surface by *in-situ* heating at 973 K under ultra high vacuum. The effective thickness and concentration of their segregated layer was estimated from the relationship between the concentration and the take-off angle in AR-XPS. AR-XPS study was also made for specimens without and with segregated surface layers which were subsequently exposed to air at room temperature. The surface segregation of chromium and nitrogen was found to considerably inhibit oxidation at room temperature, and such feature was rather distinct compared with the ferritic steel case by chromium segregation alone. These results on the surface layers were consistent with changes in the observed chemical state denoted by Fe 2p and Cr 2p due to the surface segregation.

Microstructure

Prediction of ferrite grain size after warm deformations of low carbon steel

A.Schmickl et al.

When deformation is carried out near the A_1 temperature in low carbon steels, ferrite recrystallisation appears to be the dominant mechanism in controlling the grain size. The present investigation has shown the dominance of ferrite recrystallisation at low temperatures between 665-690°C by the application of an austenite recrystallisation power law on experimentally measured grain sizes in 0.05 % C steel. Comparison has also been made between predictions using this power law and the experimentally measured grain size after deformation in the two phase $(\alpha + \gamma)$ region. The results show that the ferrite grain size is influenced significantly by the relative proportions of γ and α phases within the structure just prior to deformation. In addition the good correlation found between predicted and measured grain sizes indicates that ferrite recrystallisation dominates between 850 - 690°C. Despite this, the possibility still exists for the occurrence of a transformation induced mechanism within this temperature region.

Solubility products of titanium sulphide and carbosulphide in ultra-low carbon steels

X. Yang et al.

The equilibrium precipitation behaviour of Ti stabilised interstitial free steels was studied quantitatively. The solubility products of TiS and $Ti_4C_2S_2$ in austenite were determined with dissolution experiments. The results are as follows

$$\log[Ti][S] = \frac{-13975}{T} + 5.43$$

$$\log[Ti][C]^{0.5}[S]^{0.5} = \frac{-17045}{T} + 7.9$$

The calculated results using these solubility products agree well with other experimental results of steels not involved in the dissolution experiments. The solubility products obtained in the current work were compared with other published solubility products of TiS and $Ti_4C_2S_2$ using all known experimental data from different sources to the knowledge of the authors, and it was shown that the solubility products determined in the current work provided the best fittings with the experimental results. The influence of reheating time on the precipitation state in the steels was also investigated. It was shown that at high temperatures (*e.g.*1 150°C) equilibrium state of precipitates can be reached within one hour during reheating.

Influence of strain on induced precipitation kinetics in microalloyed steels

S.F.Medina et al.

Using torsion tests and applying the back extrapolation method, the statically recrystallized fraction of low carbon microalloyed steels containing vanadium, niobium and titanium, respectively, has been determined for different temperatures and strains. From the recrystallized fraction against time curves it is possible to draw precipitation-time-temperature (PTT) diagrams. These diagrams show that the strain does not affect precipitation kinetics in an independent manner, but that this influence is related with the microalloy content. The greater the strain applied, the shorter the incubation time of induced precipitation, but this influence diminishes as the microalloy content increases. It is also demonstrated that the incubation time is practically independent of the nature of the metal microalloy(V, Ti, Nb). In this sense, new expressions are proposed to relate the incubation and precipitation end times with the strain and the microalloy content. A model is also established for precipitation kinetics at the curve nose temperature.

Ferrite nucleation at ceramic/austenite interfaces

S.Zhang et al.

Pure polycrystal ceramics (TiC,TiN,TiO, VN, AlN and AL_2O_3) were heat-pressure-bonded to an Fe-0.1mass%C-2mass%Mn alloy and isothermally reacted below the Ae_3 temperature for the proeutectoid ferrite reaction to occur. The nember of ferrite particles per unit area of bonded interfaces was measured using Schwartz-Saltykov method and was compared with the number of particles formed at grain boundaries. VN was most effective in stimulating ferrite nucleation whereas TiO was least effective. All other ceramics showed more or less similar potencies for ferrite formation. VN is capable of forming lower energy interfaces with ferrite than other ceramics, though the possibility of V diffusion into the alloy during and after bonding may not be ruled out in this experiment. On the other hand, the least effectiveness of TiO in stimulating ferrite nucleation is possibly due to the proximity of thermal expansion coefficient to iron.