

Fundamentals of High Temperature Processes

Phase equilibria in the titanium-iron-oxygen system in the temperature range of 1173 to 1373K S.ITOH

Phase relations and the equilibrium partial pressures of oxygen in the titanium-iron-oxygen ternary system have been studied in the temperature range of 1173 to 1373K by means of a thermogravimetric method in a CO-CO₂ gas mixture and X-ray diffraction technique for the quenched samples after the equilibrium experiments. The objective of the present work is both to clarify the relation between the phase relations in the Ti-Fe-O ternary system and the equilibrium partial pressures of oxygen, and to discuss the possibility of upgrading natural ilmenite ore to a rutile substitute for extractive metallurgy of titanium.

The results are summarized as follows: The phase diagram and isobars of oxygen in the titanium-iron-oxygen ternary system at 1173, 1273 and 1373K have been determined. It was found from the present results that upgrading ilmenite (FeTiO₃) to a rutile (TiO₂) substitute is thermodynamically possible.

Both the activities of magnetite and ulvospinel show negative deviations from Raoult's law in the Fe₃O₄-Fe₂TiO₄ spinel solid solutions coexisting with metallic iron in the temperature range of 1173 to 1373K.

The conductivity and the crystallization of perovskite (CaTiO₃) from Ti-bearing blast furnace slags studied by A. C. impedance method S.WANG *et al.*

The conductivities of a Ti-bearing blast furnace slag (with 23% TiO₂) and the synthetic slag consisting of CaO-SiO₂-Al₂O₃-TiO₂-MgO were measured accurately in the temperature range of 1653-1733K by A. C. impedance method. The relationships between the conductivity and temperature were obtained as: $\ln \kappa = 14.212 - 24820/T$ for the Ti-bearing blast furnace slag and $\ln \kappa = 8.557 - 15860/T$ for the synthetic slag (unit of κ : $\Omega^{-1} \cdot \text{cm}^{-1}$) in the temperature range of 1703-1733K. Perovskite phase (CaTiO₃) could precipitate from these slags during slag cooling process. The temperature at which CaTiO₃ started to crystallize was determined as 1693K. Rate constants and activation energy for the formation reaction of CaTiO₃ were calculated based on the data of conductivity and the first order kinetic equation. Dissociation reactions of Al₂O₃ and TiO₂ could take place due to the crystallization of perovskite phase and the variation of the basicity of the slag. The rate constants and the activation energy for the dissociation reactions were also calculated.

Effect of vacuum on mixing behavior in a ladle—a watermodel study K.KRISHNAKUMAR *et al.*

Rising inert gas bubbles in a vacuum ladle experience phenomenal expansion in the top portion of the bath due to the steep variation of absolute pressure. This makes the top layers of the melt substantially more agitated than the bottom regions. The present

study is an attempt to characterize the mixing process in such a vacuum ladle by a watermodel, simulating the effect of extra stirring in the top layers of the bath. The simulation is done through a two-level blowing, in which an additional gas stream is injected into the main bubble plume at 75% of the bath height. It was found that mixing under such a simulated condition is worse than that in a bottom purged ladle, for identical total energy inputs to the bath. The study reveals that the energy imparted in the top layers of the liquid in the vacuum ladle is less effective in promoting mixing. The pattern of stirring energy input distribution along the height of the bath is an important parameter in determining the mixing behavior in a ladle, apart from the total energy input.

Kinetics of gas oxidation of liquid Fe-C-S alloys and carbon boil phenomenon H.SUN *et al.*

The decarburization and oxygen absorption rates in liquid iron droplets by an oxidizing gas were investigated at 1723-1843K. More rapid carbon oxidation was observed at lower sulfur concentration or at higher temperature. The rate of oxygen absorption by liquid iron droplets was found to be suppressed by the interfacial carbon oxidation initially, and then increased rapidly even when there was still a high content of carbon left behind in the liquid. Sulfur content of the liquid was essentially unchanged during the oxidation. These observed results are well explained by a kinetic model assuming that either the transport in gas and liquid, or the interfacial reaction are jointly controlling the process of the oxidation. A model describing gas bubble nucleation from the liquid is also proposed in the present work. The profiles of liquid composition, pressure of CO in equilibrium with the liquid, interfacial specific energy and the critical radius for gas nucleation from the liquid in the droplet were predicted with these models. These predicted results were found applicable to the interpretation of the carbon boil phenomenon during gaseous oxidation.

Ironmaking

Heat exchange in the hearth of a blast furnace operating with combined blast parameters A.FORMOSO *et al.*

Heat exchange occurs most intensively in the hearth of the blast furnace (BF) and determines metal quality, furnace productivity and operating parameters. The heat and chemical energy needed for the BF process is generated in the raceways.

This paper is dedicated to the advancement of the heat exchange theory in the hearth of a BF operating with combined blast. The heating processes of products of melting in the raceway and in the liquid bath of the hearth and the effect of pulverized coal injection (PCI) on heat exchange in the oxidizing zone and its extension are studied.

An increase in furnace productivity requires additional heat power for the heating of pig iron and slag and therefore a rise in flame temperature. PCI increases radiation in the raceways, thus permitting

BF operation with a lower flame temperature.

These theoretical conclusions are confirmed by calculations for two BFs in the Ukraine and Spain and by statistical analysis of the operation of the majority of BFs in EU countries. At one BF in Germany the effect of PCI and other combined blast parameters on the raceway extension was investigated using the laser technique.

Steelmaking

Application of the sulphide capacity concept on high-basicity ladle slags used in bearing-steel production

M.A.T.ANDERSSON *et al.*

A rigorous evaluation of the usefulness of some existing models for prediction of sulphide capacity and sulphur distribution for industrial slags at Ovako Steel AB has been carried out. The results show that the best agreement between calculated and analysed sulphur distributions is obtained by calculating the alumina activity in the slag from an expression suggested by Ohta and Suito,²⁶⁾ then using these data to calculate the oxygen activity in the molten steel, and finally by applying the KTH model⁴⁻⁶⁾ to calculate the sulphide capacity and sulphur distribution. Therefore, the conclusion is that the KTH model⁴⁻⁶⁾ is a useful tool for predictions of sulphur distributions for ladle slags.

Casting and Solidification

Surface roughness of solidified mold flux in continuous casting process K.TSUTSUMI *et al.*

Heat transfer in continuous casting mold is important to decide the surface quality of the cast slab of middle carbon steel. Many researchers have recently studied the mechanism of reducing the heat transfer between the mold and the solidified shell, and some of them have pointed out that the interfacial thermal resistance between the mold and surface of solidified mold flux has caused decreasing heat transfer.

In the present study, the surface roughness of solidified mold fluxes used for low carbon and middle carbon steel casting, Na₂O-CaO-SiO₂ and Li₂O-CaO-SiO₂ slag systems, was measured by a confocal scanning laser microscope combined with an infrared image furnace. It was found that the surface roughness was in the range of approximately 10-30 μm when the crystalline phase precipitated. Furthermore, the faster the cooling rate, the smoother the surface roughness of the solidified mold flux became. In the contrast, the surface roughness of the slag, of which critical cooling rate is faster, increased. The surface roughness of the mold flux for middle carbon steel casting became rougher than that for low carbon steel casting. As a result, the surface roughness was related to normalized cooling rate, which is the ratio of actual experimental cooling rate to critical cooling rate. The experimental data of surface roughness were fairly in agreement with calculated values on the assumption of one dimensional heat transfer in the continuous casting

mold.

Formation criterion of macrosegregation in a squeeze cast Al-7mass%Si alloy

S.M.LEE *et al.*

The formation behavior of macrosegregation in an Al-7mass%Si squeeze-cast ingot was investigated based on a series of experiments. Main process parameters such as applied pressure, pouring and die temperatures were observed to influence the solidification rate and the average temperature gradient in the squeeze-cast ingot. A criterion for the formation of macrosegregation in an Al-7mass%Si squeeze casting, $P^{1.5}G^{0.5}R^{-5.8} > 9.7$ was proposed through the empirical method. It is suggested that sound squeeze castings, free from both shrinkage defects and macrosegregation, can be obtained by means of inoculation or adequate insulation with a medium applied pressure range for practical applications.

Transformations and Microstructures

Effect of dissolved cerium on austenite grain growth in an Fe-0.20mass%C-0.02mass%P alloy

M.GUO *et al.*

The effects of dissolved cerium on the kinetics of austenite grain growth and on the grain size and grain shape distributions were studied at 1473, 1573, and 1673K in an Fe-0.20mass%C-0.02mass%P alloy containing a limited amount of second-phase particles as a function of holding time. The mean planar grain diameter (D_{mean}) for a given holding time decreased considerably with the addition of dissolved Ce up to 300 mass ppm and then decreased gradually. The parabolic law kinetics was observed and its apparent rate constant was inversely proportional to the content of dissolved Ce in atomic pct. The spatial grain size distribution obtained by the Johnson-Saltykov transformation could be best described by the log-normal distribution function and normal grain growth was observed. The $D_{\text{max}}/D_{\text{mean}}$ (D_{max} : the maximum grain diameter) value was independent of the content of dissolved Ce and holding time. The distribution of the number of grain sides was observed to be holding time-invariant and was not affected by the presence of dissolved Ce.

The effect of chemistry on the formation of ultrafine ferrite in steel

M.R.HICKSON *et al.*

A thermomechanical process has been developed to produce ultrafine (1–2 μm) ferrite grains in hot rolled steel strip. This process involves rolling the steel at or just above the austenite to ferrite transformation temperature, and was applied to a variety of steel chemistries, including plain low and high carbon grades and steels containing microalloying elements such as Nb, Ti, B and Mo. Significant volume fractions of ultrafine grains were observed in all samples. However, it was found that the chemical composition of the steel slightly influenced the morphology and volume fraction of ultrafine grains formed in the surface layers of the strip, and significantly altered the microstructure formed in the core of the strip. In plain carbon grades, the level of ferrite refinement increased slightly as carbon content increased. In the case of the microalloyed steels, those containing Nb and Ti additions produced the greatest level of refinement. The volume fraction and level of refinement of the ultrafine ferrite grains also influenced the strengths of the steels.

Effect of initial microstructure on the coarsening behavior of cementite particles

W.J.NAM

The effect of initial microstructures, martensite and bainite, on the coarsening behavior of cementite particles during tempering at 973K for medium carbon steels has been investigated. The coarsening of cementite particles in bainite proceeded more slowly than in martensite, due to the thermal stability of cementite particles in bainite. The coarsening of cementite particles proceeded by a combination of the different coarsening mechanisms. The observed coarsening kinetics in martensite were found as a combination of boundary diffusion and diffusion along dislocation for cementite particles at boundaries, and a combination of boundary diffusion and matrix diffusion for cementite particles within laths. In bainite, the coarsening was controlled by a combination of boundary diffusion and diffusion along dislocation for intergranular particles, and controlled mainly by diffusion along dislocation for intragranular particles.

In-situ observation of intragranular ferrite nucleation at oxide particles

T.HANAMURA *et al.*

"In-situ" real time observation of the ferrite nu-

cleation at nonmetallic inclusions has been successfully made at elevated temperatures with a confocal scanning laser microscope. The nucleation site, nucleation temperature, and/morphological change of the precipitates and ferrite can be sequentially determined as the phenomena occurring on the surface of steel. A polygonal ferrite starts to precipitate at an oxide particle at 1010K and a Widmanstatten ferrite starts to precipitate at a MnS particle at 967K. The degree of super cooling for austenite-ferrite transformation is found to be in good agreement with the prediction by a thermodynamic calculation.

Mechanical Properties

Micromechanical investigation of the hot ductility behavior of steel

C.M.CHIMANI *et al.*

Using a periodic microfield approach a micromechanical study is presented, which is capable to describe the ductility losses due to a film like ferrite precipitation in the high temperature region of iron based alloys by considering the two phase microstructure close to phase transformation temperatures and explicitly accounting for the elasto-plastic material properties of each present phase.

For the temperature range close to the A_{c3} temperature it will be demonstrated that the hot ductility behavior is directly correlated to the volume fraction of ferrite which develops along the austenitic grain boundary and the global strain rate of the specimen.

Mechanisms of cyclic plasticity of a ferrite-bainite 2 1/4Cr1Mo steel after long-term service at high temperature

J.-B. VOGT *et al.*

LCF tests were carried out at 565°C on a ferrite-bainite 2 1/4Cr1Mo steel that has been taken from a power plant component after a 160000 h service time. Before fatigue, a detailed preliminary analysis of the microstructure was first performed not only in terms of precipitates but also in terms of dislocation cell subboundaries present in the bainitic grains. Strain cycling globally led to a softening of the alloy which can be preceded by a hardening period depending on the strain amplitude. A fatigue cellular structure developed in the ferritic grains whatever the strain level. In the bainite, it was possible by CBED to show a rotation of the preexisting cells as indicated by the orientation measurements. The mechanisms of cyclic plasticity of the 2 1/4Cr1Mo steel is thus explained by considering the individual behavior of each phase.