

Fundamentals of High Temperature Processes

Solubility of MnS in Fe-Ni alloys as determined by *in-situ* observation of precipitation of MnS with a confocal scanning laser microscope

N.YUKI *et al.*

Solubility of MnS in Fe-Ni alloys has been investigated by "*in-situ*" observation with a confocal scanning laser microscope of specimens with various Mn, S and Ni contents which were heated and cooled in an infrared image furnace. Precipitation behavior of MnS at the surface of the specimens on cooling was monitored on a CRT and was recorded on videotape. Most MnS precipitates are found to precipitate on alumina inclusion particles and grow in triangular (pyramidal) or rod-like shape. From precipitation temperatures obtained by the "*in-situ*" observation, the equilibrium constant of the reaction $\text{MnS} \rightleftharpoons \text{Mn} + \text{S}$ is determined as $\log K = \log[\% \text{Mn}][\% \text{S}] f_{\text{S}}^{\text{Mn}} = -9.420/T + 3.67$, at $T = 1329 \sim 1493$ K for Fe-42mass%Ni alloy. The K value for γ -Fe at 1438 K is in good agreement with the previous study by Turkdogan *et al.*, and Ni is found to increase the solubility of MnS.

Ironmaking and Reduction

Gas-solid reaction model for non-spherical iron oxide

H.W.KANG *et al.*

Iron oxide pellets of various shapes are reduced from hematite to magnetite with CO-CO₂ gas mixture to investigate the shape effect on the gaseous reduction rate of an iron oxide pellet. Based on the observation result of the section of partly converted pellets, a model of the mixed-control kinetics for a non-spherical iron oxide is proposed. A determination method of the rate parameters included in this model is presented. Applicability of this model is reviewed comparing to one of existing models for non-spherical particle. For derivation of the mixed-control rate equation for a non-spherical iron oxide, the concept of non-spherical radius is introduced.

Steelmaking and Refining

Effects of tundish cover powder and teeming stream on oxidation rate of molten steel in tundish

K.SASAI *et al.*

The oxidation rate of the molten steel covered with the tundish cover powder and the molten steel being teemed was measured and the reaction mechanism was investigated as a basic study to quantify the oxidation rate of molten steel at different parts in an actual tundish.

The oxidation rate of the molten steel covered with the tundish cover powder is proportional to the partial pressure of O₂ gas in the gaseous

phase and the reciprocal number of thickness of tundish cover powder and can be explained by mass transfer control model of O₂ gas in the layer of tundish cover powder.

The oxidation rate of stirred molten steel and molten steel being teemed is proportional to the partial pressure of O₂ gas in the gaseous phase and the 0.45th power of the stirring energy per unit area and can be rationally explained by a control model of mass transfer of O₂ gas in the gaseous phase in which an increase in the reaction interface area due to stirring is considered.

Casting and Solidification

Modeling the behavior of Al₂O₃ inclusions during the dendritic solidification of steel

H.SHIBATA *et al.*

Starting with a distribution of single-particle alumina inclusions, estimates of their collision frequencies and the number concentrations of two- and three-particle clusters in the interdendritic liquid during solidification were made. The alumina clusters possibly serve as pore-nucleation sites, so their number concentrations that form during solidification are of interest. We also show that the smaller alumina inclusions are not entrapped in the dendritic solid during solidification, based on estimates of the interdendritic solidification rates and empirical data on the engulfment of Al₂O₃ inclusions by solidifying steel. Engulfment by the interdendritic liquid, however, is enhanced by the gradients of the concentrations of oxygen and sulfur in the interdendritic liquid during solidification. These elements are surface active on the liquid-steel/alumina interface and, in turn, introduce very strong capillary forces on the interdendritic alumina inclusions.

Development of double and single hot thermocouple technique for *in situ* observation and measurement of mold slag

Y.KASHIWAYA *et al.*

To overcome the limitations of differential thermal analysis (DTA) and direct casting experimentation in the measurement and understanding of the solidification phenomena of mold slags, the double and single hot thermocouple techniques (DHTT and SHTT) for the direct observation and measurement of mold slag crystallization were developed. These methods enable the solidification and melting process of transparent slags to be observed "*in situ*" under conditions where the temperature or temperature gradient can be measured and controlled. The SHTT allows a sample to be subjected to rapid cooling rates or to be held under isothermal conditions. The DHTT allows large temperature gradients to be developed between the two thermocouples and allows a simulation of the transient conditions which can occur in the

infiltrated slag film that occurs between the mold and the solidifying shell in the mold of a continuous caster. By these techniques both isothermal and non-isothermal phenomena can be studied.

A number of mold slags are optically transparent or translucent at steelmaking temperatures while the crystalline phase which precipitates upon cooling is opaque and can be clearly observed using optical microscopy. Thus the SHTT and DHTT are connected to an image capturing and analysis system that allows the onset and growth of the opaque crystals which precipitate from the slags to be documented. The development and application of these techniques to mold slag crystallization will be discussed in this paper.

An investigation of the crystallization of a continuous casting mold slag using the single hot thermocouple technique

Y.KASHIWAYA *et al.*

The conditions under which crystallization develops in a mold slag must be understood in order to select or design a mold flux for use in the continuous casting of steels. In this paper, the crystallization of an industrial mold slag was quantified using a single hot thermocouple technique which, when combined with a video camera based observation system, allowed observation of the onset and growth of the crystals which were precipitated from the melt. The beginning of crystallization was determined by direct observation and the growth rate of crystals were measured by frame by frame image analysis of recordings of the progress of crystallization. Isothermal experiments were performed at different temperatures and a Time-Temperature-Transformation (TTT) diagram was determined for this industrial mold slag. X-ray diffraction of quenched samples was used to determine the type of crystalline phases that were precipitated. The TTT diagram was divided into two separate regions which corresponded to the precipitation of dicalcium silicate (Ca₂SiO₄) at temperatures over 1050°C and of Cuspidine (Ca₄Si₂O₇F₂) at temperatures below 1050°C. The evolution crystal fraction was described by Avrami's equation. This work indicates that industrial mold slags are easily undercooled, that crystallization occurs throughout the melt, that crystals grow initially as equiaxed dendrites and that the onset of crystallization is a function of cooling rate and must be described by either TTT or CCT curves.

Surface Science and Technology

Development of a high speed cold rolling oil with mill cleanliness property

S.Y.HAN *et al.*

The purpose of this study was to develop a cold rolling oil with lubricity and mill cleanliness property under the rolling conditions of

high reduction ratio and high rolling speed. Seven kinds of test oils composed of various base oils, emulsifiers, EP additives, anti-oxidants *etc.* were blended. Evaluation of lubricity and anti-seizure property of the test oils was carried out with a laboratory scale rolling mill, where the contact conditions between work roll and strip are very close to those of an actual cold rolling mill. Laboratory evaluation for dispersibility, anti-contamination property, rust prevention property, residual carbon, *etc.* were carried out with several testers such as a long-term circulation tester, the oxidation stability tester and the Conradson residual carbon tester. Finally, a new high speed cold rolling oil with good lubricity and mill cleanness property was developed by referring to the previously developed high speed cold rolling oil.

Microstructure

Effect of deformation and cooling rate on the microstructures of low carbon Nb-B steels

D.Q. Bai et al.

The transformation behaviours and microstructural characteristics of three B-containing steels were investigated. In particular, the effects of deformation in the no-recrystallization temperature range and cooling rate were studied by means of compression tests. It was found that over a large cooling rate range (from 1 to 50°C/s), the Mo-Nb-B steel exhibits microstructures consisting of a mixture of plate-like or lath-like ferrite with retained austenite or martensite (*i.e.* M/A) islands. This is basically a low carbon bainitic microstructure, and can be identified as B_3 in the Bramfitt and Speer classification system. The lengths of the ferrite laths increase and the widths decrease as the cooling rate is increased. The shapes and distributions of the M/A islands change from being blocky and randomly distributed to fine and more aligned, as the cooling rate is increased. Also, the lengths of the bainitic ferrite laths are shortened by heavy deformation in the no-recrystallization temperature range. The microstructures of the Nb-15B and B-only steels are

basically polygonal ferrite at low cooling rates; however, the fractions of bainite in these two grades increase with cooling rate. The minimum cooling rate required for avoiding polygonal ferrite formation during continuous cooling are much higher in these two grades than in the Mo-Nb-B steel.

Deformation microstructure and nucleation of recrystallization in hot-deformed single crystals of 18%Cr ferritic steel

N. TSUJI et al.

Static recrystallization of the hot deformed single crystals with [001], [111], [133] and [135] initial orientation of an 18% Cr ferritic stainless steel was studied. It was clarified that the hot-deformed microstructures and the recrystallization behaviors strongly depend on the initial orientation. The [001] crystal showed coarse and diffuse subgrains after hot-compression, the [111] and the [135] crystals formed relatively fine and uniform subgrains, and a number of the deformation bands elongated perpendicular to the compression axis developed in the [133] crystal. The [001] crystal was extremely hard to recrystallize and showed no recrystallization after a long time annealing. The [111] and the [135] crystals were relatively hard to recrystallize. The enhanced recrystallization along the deformation bands occurred in the [133] crystal, and the recrystallized grains had the orientations between those of the matrix and the deformation bands. The dislocation density, *i.e.*, the driving force for static recrystallization, in the hot-deformed subgrain structures were quantitatively evaluated on the basis of the detailed TEM observations. Although the dislocation density in the [001] crystal which showed no recrystallization was lower than those of the other orientations, that of the [133] crystal which showed enhanced nucleation was similar to that of the [111] crystal which was relatively hard to recrystallize. That is, the dislocation density in the deformed matrix does not necessarily correspond with the easiness of nucleation. EBSP measurements clearly showed that the narrow regions (transition bands) between the deformation bands and the

matrix in the [133] crystal bear large misorientations about 50 degrees. It is concluded from those results that the large local misorientation in the deformation microstructure does be important for the nucleation of recrystallization and it is generally treacherous to discuss the nucleation problem only on the basis of the macroscopic and averaged information, such as the mean dislocation density, of the deformed state.

Social and Environmental Engineering

Positive growth of phytoplankton under conditions enriched with steel-making slag solution

Y. NAKAMURA et al.

The growth ability of 12 species of phytoplankton was examined in culture media enriched with steel-making slag solution at various concentrations. Since a highly significant linear regression of the *in vivo* fluorescence (IVF) of cell suspension against absolute chlorophyll *a* concentration was established, the growth ability was determined quickly by IVF. Under the enriched conditions all the species examined showed positive growth, although in different manners. Based on the specific differences in the optimal concentration of the slag solution, 12 organisms could be divided into four groups: (I) the organisms which grow best under the highest enrichment (100%), (II) those which grow best with intermediate enrichment, but not in 100% enrichment, (III) those which grow best under enrichment lower than 60%, and (IV) those which respond inconsistently to enrichment but often grow better under enrichment. These results indicate that the slag solution has positive effects for the growth of phytoplankton, so that the slag will be utilized as nutrients in cultures for algae. On the other hand, the growth of all the four groups enhanced by the enrichment with the slag solution never exceeded the growth enhanced in an ideal culture medium, indicating that the enrichment with the slag solution can hardly be a cause of the red tide, if the enrichment is done in nature.