Fundamentals of High Temperature Processes

Small-angle neutron scattering measurements on SnO_2 particles suspended in liquid Sn-S systems

T.IIDA et al.

Small-angle neutron scattering measurements were carried out on liquid Sn-0.4 mol% SnO_2(solid spherical particle)-1.1 at% S, Sn-0.4 mol% SnO_2 and Sn-1.1 at% S systems at 723 K. The scattering intensity for Sn-SnO_2 system is proportional to the parameter, Q^{-4}, while the scattering intensity for Sn-SnO_2-S system is lower, showing nearly Q^{-3} dependence. To analyze them, the scattering intensity has been calculated for Sn-SnO_2 and Sn-SnO_2-S systems with various particle sizes and thicknesses of the surface layer. For Sn-SnO_2-S system, the best fit with the experimental data has been obtained for a particle size of 4μm and the surface layer thickness of 100 Å, consisting of S.

Interfacial tension between molten iron and CaO-SiO_2 based fluxes

H.SUN et al.

Flux-metal interfacial tension has been examined by X-ray photography of a metal drop melted in a molten flux. The experiments were carried out at 1 580°C using a zirconia crucible with low solubility in the fluxes. The systems used in the investigation were as follows:

Metal phase: Fe-O alloy, oxygen content in the alloys varied from 0.002 to 0.070 mass%

Flux phase: Ternary system: CaO-SiO_2-$M_x(F, O)_y$, where $M_x(F, O)_y$ represents NaF, CaF_2, Al_2O_3, Na_2O, MgO, Li_2O or ZrO_2 and concentrations varied from 2 to 40 mass%.

Multicomponent system: CaO-SiO_2-Al_2O_3-Fe_2O_3-Na_2O-NaF-CaF_2-MgO-Li_2O-ZrO_2

The interfacial tension was observed to increase with increasing NaF, CaF_2, Na_2O, MgO or Li_2O contents, while only minor changes in the values were observed with varying Al_2O_3 or ZrO_2 contents in CaO-SiO_2 or CaO-SiO_2-Al_2O_3 systems. The interfacial tensions between flux and molten iron decreased with increasing oxygen activity in iron,

$$\gamma = \gamma_0 - 0.324\ln(1+116a_o)$$

Effect of titanium addition on the formation and distribution of MnS inclusions in steel during solidification

K.OIKAWA et al.

Effect of titanium addition on the size and dispersion of MnS inclusions in Fe-0.1C-1Mn-0.02S(mass%)base alloys has been investigated by microscopy. Titanium addition brings about a marked decrease in the size of MnS inclusions which are otherwise large and globular in Ti-free specimens. The formation mechanism of MnS inclusions is discussed on the basis of phase diagram information and thermodynamics of particle engulfment during solidification. It is shown that the reduction in size of the MnS particles consequent on Ti addition is directly the result of successive nucleation events involving (Ti, Mn) O and MnS at the solid/liquid interface of iron.

Ironmaking and Reduction

Analysis of three dimensional structure of iron-ore sintercake

M.NAKANO et al.

Three-dimensional structure of iron-ore sintercakes, which are prepared by pot test (90 mm-dia. ; 400 mm-height) with varying the location in bed and Al_2O_3 content, has been investigated with the use of an X-ray CT and a three-dimensional image analyzing system. It has revealed that sintercake basically consists of a continuous plate-shaped matrix including numerous closed pores of under-2 mm diameter and a continuous inter-communicating pore. Moreover, the shape of the matrix/pore in the lower part of the bed becomes round, though few changes by Al_2O_3 can be detected.

Iron carbide synthesis by reaction of iron ore with H_2-CH_4 gas mixtures

S.HAYASHI et al.

Particles of hematite ores in a porcelain boat were reacted at 873~1 273 K by H_2-CH_4 mixtures having low sulfur activities a_s based on Fe/FeS equilibrium where metallic iron remained stable. In the tests without sulfur, much free carbon appeared beside metallic iron and iron carbide. The free carbon increased with temperatures. In the tests with sulfur, nearly one hour reaction could convert their particles mostly to iron carbide such as Fe_3C, especially favorable in a_s=0.1~1.0 at 1 173~1 223 K. The conversion yield was sensitive to inlet flow volume ratio H_2/CH_4 and ore type, while the authors' previous test in H_2-CO gas mixtures had already indicated their insensitivity.

Admixing hydrocarbons in raw mix to reduce NO_x emission in iron ore sintering process

C.-L.MO et al.

The traditional de-NO_x processes in iron ore sinter plants, power plants or in refineries is to treat the waste gas by the Selective Catalytic Reduction (SCR) process or Selective Non-Catalytic Reduction (SNCR) process which removes the nitrogen oxides from the flue gas. Space and huge capital requirements are needed for installing of such de-NO_x facilities. This study takes a different approach, aiming at reducing the formation of NO_x during sintering rather than treating the waste gases. Our preliminary experimental findings showed that NO was drastically decreased by introducing hydrocarbons into the sinter mix. Rice husk and sugar had the potential to improve the sinter bed permeability and shorten the high temperature duration time in the combustion zone. The encouraging results showed that the NO_x concentration was decreased from 223 to 160 ppm, or emission was decreased from 533.8 g/t.sinter to 283.3 g/t.sinter by 1 % sugar addition and the productivity was increased from 37.5 to 45.4 t/m²/24hr. The sinter qualities of Tumbler Index (ISO+6.3 mm %) was kept the same, the RDI was improved from 31.5 to 27.3 %.

Casting and Solidification

Reduction of macrosegregation by applying DC magnetic field at the final stage of solidification

M.NAKADA et al.

A new technique using a static magnetic field (DC field) for the modification of macroscopic segregations and porosities in continuously cast billets or blooms has been investigated. If the DC field is applied to the crater end area in a strand, numbers of the V-segregations and porosities could be expected to result in a decrease, since the molten steel flow in the semi-solid region seems to be modified by the DC field. This phenomenon was observed when the magnetic flux density of the DC field of 0.2 to 0.42 Tesla was applied during the solidification of the center of the cast ingots, where the solid fraction had values of 0 to 1.0, which is in the final stage of solidification. In addition, the application of the DC field to the center part of the ingot with a solid fraction range, 0 to 0.3, showed similar effects. Hence, the application of a higher magnetic flux density, when the ingot contains a low solid fraction at the center part, was found to result in a decrease of the V-segregation and porosity. It is suggested that the DC field homogenized the fluid flow velocity in the semi-solid region at the center part of the ingot.

The improvement of surface quality of continuous rheocast bars of steel and high melting point alloys

K.E.BLAZEK et al.

A new continuous rheocasting process for steels and high temperature alloys has been developed by Inland Steel incorporating a dual chamber casting machine utilizing separate electromagnetic stirrers around each chamber. Initial casts on the rheocaster were plagued by breakouts and very rough as-cast surface morphology. The mechanism for solidification and formation of cast surface morphologies on as-rheocast bars has been determined and verified by comparing predicted surface morphologies to actual surface morphologies. The mechanism was then used to develop new withdrawal patterns to eliminate sticker breakouts and obtain good surface quality.

In-situ measurement of fracture strength of solidifying steel shells to predict upper limit of casting speed in continuous caster with oscillating mold

M.SUZUKI et al.

Preventing crack formation of solidifying steel shell at increasing speed in continuous slad casting operation is a prerequisite to increase the ratio of hot charge rolling and hot direct rolling of cast slabs. Crack formation is influenced by mechanical properties of the steel shell near its solidus temperature. Thus, fracture strength of solidifying steel shells containing 0.004 to 0.70 mass% C has been measured *in-situ* by using a method similar to "Submerged Split Chill Tensile (SSCT)" test by Ackermann, Kurz and Heinemann. The fracture strength at an early stage of solidification, when the shell thickness is 3 to 5 mm, has been found to be 1 to 3.5 MPa which is lower than that determined by conventional hot tensile tests, since the crack initiates at and propagates in interdendritic region in the shell in the *in-situ* SSCT test. Comparing the fracture strength of the shell with the frictional force at the shell/mold interface, upper limit of casting speed of slab caster is calculated to be around 8.5 m/min.

Instrumentation and Control System

Spiked parallel plate creep/rotational viscometer and its characteristics

Y.SHIRAISHI et al.

An ultrawide range viscometer which is based on a combination of the indentation, parallel plate and rotating plate methods has been developed. A cylindrical glass sample is placed between spiked and smooth discs and pressed by a suitable load and its deformation rate is measured under an ascending temperature process. At first, the spike penetrates into a glass and then the surface of spiked disc causes a bulky creep of the sample. On melting of the sample, the concentric rotating method is used in which a disc is rotated at adequate speed and the torque exerted on the disc is measured. Thus, a wide range viscosity, extending from 10^{12} to 10^{1} Pa·s, can be sequentially determined by the measurements of the indentation rate, creep rate and rotational torque. Since the principles and a mechanism of this viscometer are rather simple, the absolute value of the sample viscosity can be determined, at least to the right order, without any calibration using standard reference materials.

The reproducibility of the results was demonstrated by the measurements, covering the glassy to molten states, of polymer glasses up to 500 K, and of boronoxide and pyrex glasses up to 1 270 and 1 470 K, respectively.

Development of recycling system for mixed nitric acid and hydrofluoric acid sludge from the stainless steel pickling process

M.ITO et al.

The sludge produced from the pickling of stainless bands settles to the bottom of the pickling tank and becomes an impediment to the operation. In this research, a very high concentrations of Cr, Ni, and Fe were found in the sludge. In particular, the concentration of Cr was more than 40 mass%. It was also found that the particle size of the sludge is as small as 9.2 μm. The diameter increases by coagulation and the sedimentation velocity of the sludge is 1.4 m/h.

Based on these results, a study was made on an ejector capable of preventing the sludge precipitation in the pickling tank and moving the sludge, and a sedimentation tank where the sludge would precipitate.

First, 14 groups of ejectors were installed on the two sides of the pickling tank. Two circulation tanks connect with the pickling tank and each group of ejectors was installed in different circulation tanks. Continuous action of the ejectors causes the sludge to remain afloat and prevents it from settling out in the pickling tank. The sludge is moved to the circulation tank, which is also equipped with the same type of ejectors as the pickling tank to prevent the sludge from settling.

Next, precipitation and separation of the sludge are performed in this sedimentation tank. After separation in the sedimentation tank, the sludge was neutralized by mixing with hydrated lime using kneading device. The neutralized sludge is loaded into a lugger bag and can be used as a raw material for steel making.

Analysis and Characterization

Measurement of normal spectral emissivity of liquid copper

K.NAGATA et al.

The normal spectral emissivity of copper in solid and liquid states was measured at 1 273 to 1 673K with wavelength during 400 to 850 nm. The ratio of radiation intensity to that at a reference wavelength of 650 nm was measured in order to avoid the difficulty of simultaneous measurement of the radiation intensity from a black body. The emissivity of copper increases in solid state and decreases in liquid state with increasing temperature and decreases with increasing wavelength in both states. At the melting point of 1 358 K, the emissivity at 650 nm discontinuously increases from 0.123 in solid to 0.143 in liquid.

Surface Science and Technology

Morphology of electrodeposited Zn/Fe crystals

Y.OHMORI et al.

Zn/Fe alloy electrodeposition on a low carbon steel sheets has been examined mainly by means of scanning electron microscopy and X-ray diffraction. The results obtained are as follows:

The crystal structure and the morphology of the film deposited in a low Fe bath changes from granular η/Γ mixed phases, to pyramidal η-phase crystals and then to layered hexagonal η-phase plates with increasing current density. The initial deposits on the substrates, however, are layered hexagonal η-phase plates at all the current densities examined. The final morphology is determined by the deposits on these η-phase crystals. The c/a ratio of η-phase varies from 1.87 to 1.63 with increasing Fe concentration in the crystals. The morphological change of η-phase crystals can be explained in terms of the atomic configurations on both $(0001)\eta$ and $\{1\bar{1}00\}\eta$ planes and the c/a ratio.

In the case of a high Fe bath, the deposited film is varied from granular η/Γ to cuboidal Γ/Γ_1 mixed phases with increasing current density.

Physical and Mechanical Properties

The susceptibility to the hydrogen embrittlement of low alloy Cr and CrMo steels

M.GOJIC et al.

Low alloy Cr and CrMo steels have been studied to determine their susceptibility to hydrogen embrittlement. The steels were quenched at a constant cooling rate of 30 Ks^{-1} and tempered at 673 and 973 K. Hydrogen charging of steels was carried out in 0.5 M H_2SO_4 solution without and with addition of propargylic alcohol as corrosion inhibitor. In spite of the current density of 2-3 $mAcm^{-2}$ and the applied load of 40 % yield strength was found that the steels tempered at 673 K were highly sensitive to hydrogen embrittlement. The steels tempered at 973 K showed significantly higher resistance to hydrogen embrittlement. In spite of higher strength, the CrMo steel showed higher resistance to hydrogen embrittlement than the Cr steel. The fracture of steels was initiated at the second phase particles followed by transgranular fracture from iron carbide or iron-manganese sulphide inclusions. Since the inclusion distributions are similar in both steels, the enhanced resistance of CrMo steel to hydrogen embrittlement is due to finer prior austenite grain and presence of Mo_2C in the ferrite matrix. With the addition of propargylic alcohol in 0.5 M H_2SO_4 solution the resistance of steels to hydrogen embrittlement was increased and fracture surface showed mostly dimple fracture.

Improvement of omega method for creep life prediction

K. MARUYAMA et al.

Omega method has been proposed for predicting rupture life from creep strain ε-time t data. The method is based on a linear relation between logarithm of creep rate $\dot{\varepsilon}$ and strain, namely a creep curve without the primary and secondary creep stages. Such a linear relation, however, seldom holds in real creep data. In this paper, the original equation is modified to the following form:

$$\varepsilon = \varepsilon_0 + \frac{1}{\Omega}\{\ln(1+\xi t) - \ln(1-\eta t)\}$$

where $\varepsilon\infty$, Ω, ξ and η are parameters characterizing a creep curve. The first and second terms in the parentheses describe primary creep and terti-ary creep, respectively. The equation is applied to ferritic steels. The four parameters of the equation can uniquely be determined for a creep curve with a curved ln $\dot{\varepsilon}$ -ε relation. The equation can well reproduce creep curves with a prominent primary creep stage. Because of the high reproducibility, the modified equation can predict rupture life with higher accuracy at an earlier stage of creep than the original equation.