Fundamentals of High Temperature Processes

Viscosities of high temperature systems-a modelling approach

S.SEETHARAMAN et al.

A mathematical model for estimating the viscosities of multi-component metallic and ionic melts at high temperatures is presented. The reliability of the model in extrapolating the viscosity data as a function of temperature and composition has been demonstrated in the case of some metallic and slag systems. A correlation between the Gibbs energy of activation for viscosities and the Gibbs energy of mixing in the case of binary metallic systems is described. Preliminary results of the experimental measurements of viscosities of the system $CaO-FeO-SiO_2$ are presented.

Ironmaking and Reduction

Tuyere level coke characteristics in blast furnace with pulverized coal injection

J.-K.CHUNG

Coke in the blast furnace experiences great changes in their properties during the blast furnace operation. Pulverized coal injection (PCI) into the blast furnace through tuyeres together with oxygen enrichment affects coke properties and blast furnace operation. Using coke sampler at tuyere level, coke samples were collected and analyzed at various coal injection rates in the both conventional and co-axial oxygen enrichment. With the help of information obtained from coke sampling results, it is known that alkali affects the coke properties, CSR′ and CRR′, in bird's nest and deadman but, in bosh and raceway, DI′ of the coke is varied with the operation conditions. Also, it is found that gas permeability resistance index in lower part of blast furnace (LK) and mean size of coke at tuyere level were predicted and matched well with the measurements.

Steelmaking and Refining

Shift of the absorption edge for the charge transfer band in slags containing iron oxides

M.HAYASHI et al.

The absorption edge shift for the charge transfer band has been investigated through absorption coefficient measurements on $Fe_2O_3-CaO-SiO_2$, $Fe_2O_3-CaO-SiO_2-Al_2O_3$ and $Fe_2O_3-Na_2O-SiO_2$ slags. The absorption edge was found to move slightly to higher wavelengths with increasing Fe_2O_3 content, but shifted markedly to higher wavelengths with increasing basicity *i.e.* $(\%CaO)/(\%SiO_2)$ and $(\%Na_2O)/(\%SiO_2)$ ratios and Al_2O_3 content. This absorption edge shift has been considered from the viewpoint of the ion refractivity of oxygen and it is proposed that the absorption edge shift is associated with changes of the electron donor power of oxygen ions.

Casting and Solidification

Attack of submerged entry nozzles by mould flux and dissolution of refractory oxides in the flux (Review)

A.F.DICK et al.

Research on mould flux attack of oxide-graphite submerged entry nozzle refractories is reviewed and discussed in light of recent work by the authors. There is general agreement that the mechanism must invole attack of both the oxide and the carbon phase, but there is some uncertainty about the process of attack of the carbon. Some workers have suggested dissolution in the steel but some recent work shows that oxidation has an important role to play. There is some debate over the importance of surface tension driven stirring in a system where forced convection rates are fairly high. Additives such as metallic silicon accelerate the breakup of zirconia grains but also appear to protect the carbon bond. Dissolution of the oxide phase is the predominant rate determining step and the relationship between diffusion refractory oxides and mould flux as viscosity is consistent with the relationship between attack and flux viscosity.

Improvement of the initial stage solidification by using mild cooling mold powder

M.KAWAMOTO et al.

The initial stage of solidification for continuous casting is very important in optimising the surface quality of steel. It is well known that hypo-peritectic steel has problems with longitudinal cracking due to shrinkage resulting from the $\delta \rightarrow \gamma$ transformation. High speed continuous casting, with a speed range of 4-5 m/min, suffers from the same problem. For a round-shaped billet caster, the shape of the mold cross section is at a disadvantage with regard to longitudinal cracking. In this study, mild cooling mold powders were developed in order to improve the surface quality of high speed casting slabs and round-billets. The results can be summarized as follows; 1) High CaO/SiO_2 ratio mold powder with a high solidification temperature is most suitable for a slab caster. 2) Low CaO/SiO_2 ratio mold powder with a high solidification temperature is most suitable for a round billet caster. 3) The effect of radiation in liquid powder film is bigger than solid powder film.

Analysis and Characterization

AFM study on morphology evolution of zinc electrodeposits

K.KONDO et al.

Nano-size growth of zinc electrodeposit is studied by using atomic force microscopy (AFM). The $(0001)\eta$ and $\{10\bar{1}0\}\eta$ of hexagonal plate crystals are aligned parallel to the steel substrate with Sn^{++} as additive. An AFM cantilever is placed on these planes in order to focus the nano-size growth image on these planes.

The $(0001)\eta$ consists of both 30 nm of granular crystals and alignments of these granular crystals, *i.e.* steps. These steps grow laterally as a result of the embedment of zinc ion clusters to the kinks of steps. The $\{10\bar{1}0\}\eta$ and initial deposit also consist of these granular crystals.

The initial zinc deposits are made up of the edges of hexagonal platelet crystals oriented ten to twenty degree from the substrate. The $(0001)\eta$ of hexagonal platelet crystals becomes parallel to the substrate as the deposit grows with Sn^{++} as additive. The $\{10\bar{1}0\}\eta$, on the other hand, becomes parallel to the substrate without Sn^{++} as additive. These changes in the texture are caused by the locations of nucleation sites of the steps on the $(0001)\eta$.

Forming Processing and Construction

Influences of feed and cross angle on rotary forging effects and redundant shear deformations in rotary piercing process

C.HAYASHI et al.

It was in 1967 that Sumitomo Metal Industries Ltd. started its research and development efforts of an improved rotary piercing mill in full swing. In 1983, its first product was put into practice at the small-diameter seamless steel tube plant in the Wakayama Steel Works. Since then, the field operation at this plant has been successfully carried out.

The rotary piercing mill employed at the above plant has the arrangement that cone-type rolls supported at both ends are used as the main rolls of which axes are inclined and crossed so that piercing may proceed at a high feed and cross (toe, cone) angle, with the disc rolls adopted instead of the plate guide shoes.

Though several reports on this cone-type piercing mill have been published, they are rather fragmentary and leave something yet to be clarified. Furthermore, the recent progress in our research and development has resulted in the concept of "the new super piercer" which allows expansion piercing. This new super piercer will be employed as the core technology of a new medium-diameter seamless steel tube plant now under construction scheduled to operate in 1997.

First of all, the influences of the feed and cross angle on the rotary forging effects and redundant shear deformations are summarized in this paper.

Influences of feed and cross angle on inside bore and lamination defects in rotary piercing for materials with poor hot workability

C.HAYASHI et al.

A cone-type piercing mill has been devel-

oped for piercing the materials with poor hot workability. This piercing mill is called "the super piercing mill" in Europe and America. This mill has cone-type main rolls supported at both ends with their roll axes inclined and crossed so as to enable piercing at a high feed and cross angle. This configuration is based on the following principles: by rendering the material more ductile than its mother material in front of the plug, any possible cause of the initiation of inside bore defects can be eliminated; and, at the same time,by releasing the redundant shear stress field during piercing process, it is possible to eliminate any possible cause of the propagation of inside bore defects. In order to ensure the best performance of the rotary piercing, disc rolls have been adopted instead of plate guide shoes. Piercing experiments were carried out using test materials with poor hot workability, such as continuously cast round billet, stainless steel, high alloy steel and Pb-S free cutting steel, with the feed and cross angle changed in various ways. The influences of the feed and cross angle on the inside bore and lamination defects were studied in detail. Furthermore, piercing experiments under high feed and cross angles were carried out with titanium, titanium alloy, zirconium alloy, nickel and nickel alloy in order to confirm the effects such a high-angles piercing.

Surface Science and Technology

Characterization and corrosion behaviour of laser surface alloyed Ni-Cr-W-Mo-Cu-C-B coatings

M.C.GARCIA-ALONSO et al.

A microalloyed steel was precoated with three different thicknesses of Ni-Cr-W-Mo-Cu-C-B powder and laser-surface-alloyed in order to achieve a corrosion-resistant surface alloy. In general, laser treated alloys showed good adherence and considerable penetration into the base material, which varied with laser treatment conditions and initial coating thicknesses. Under conditions studied, laser treated alloys presented a dendritic structure. The degree of dilution increased as both laser scanning rate and initial coating thickness decreased. The lowest iron content at the surface was reached for samples with a 1 000 μm initial coating thickness and laser treated at the maximum scanning rate 0.054ms^{-1}. This low iron content jointed to a high content of chromium and nickel on the surface gave rise to the formation of a protective and stable passive layer that implied a high corrosion resistance in $Na_2SO_4$0.1 M. The samples with 250 and 500 μm coating thicknesses presented in most cases a martensitic transformation within the coating due to the high degree of dilution between coating and base material decreasing drastically the corrosion resistance of the melted coating.

Oxidation of type 304 stainless steels under simulated annealing conditions

B.OZTURK et al.

Stainless steel processing often involves an annealing step, which is most economically performed in atmospheres formed by the combustion of natural gas and air. During the annealing process the surface of the steel reacts with oxidants such as O_2, CO_2 and H_2O in the furnace atmosphere to form a scale layer. The scale formation is undesirable due to its effect on yield and surface quality. In the present work, an investigation was carried out to determine the rate of scale formation of type 304 stainless steel under short-time annealing conditions. A thermogravimetric apparatus was used to study the rate of scale formation. Gas compositions were chosen to simulate different ratios of air/CH_4.

A protective layer forms on the samples that are oxidized in simulated gas mixtures corresponding to air/$CH_4 \geq 11$ at 1 373 K. The layer breaks down after about 12min of reaction time due to formation an iron oxide layer on the surface. It was found that the protective layer is composed of small crystals of spinel, Cr_2O_3, FeO.

A non-protective layer forms on 304 type stainless steel when it is annealed in atmospheres corresponding to air/$CH_4 \leq 9.53$ at 1 373 K. The initial rate of scale formation is much faster when type 304 stainless steels are annealed in atmospheres corresponding to air/$CH_4 \leq 9.53$ at 1 373 K. The rate of scale formation is much faster when an iron oxide layer forms on the samples. It was found that an iron oxide layer forms at the initial stage of oxidation when air/$CH_4 \leq 9.53$. The scale is composed of two layers. The outer layer is almost pure wustite when air/$CH_4 \leq 9.53$. The inner layer is spinel in the form of small nodules like crystals. The iron oxide layer detaches from the samples during cooling. The outer layer may contain small amounts of Fe_2O_3 and Fe_3O_4 when air/$CH_4 \geq 11$ for longer periods (~20min). The oxidation occurs at the gas-scale and scale-metal interfaces. The over-all rate of scale formation is controlled by both diffusion of iron upwards and diffusion of oxidizing agents through cracks and microchannels.

Microstructure

Structure of a low carbon Al-killed/Ti-added steel

R.MENDOZA et al.

A low carbon Al-killed/Ti added steel was processed in a Mexican steel company as a part of a research program which has the scope of developing ultra low carbon steels for automotive applications. Microstructural characterization of slab in the as-cast and reheated conditions prior to the rolling operations is presented, giving emphasis to the nucleation of TiN on existing AlN particles, evidence of this behaviour is presented.

Physical and Mechanical Properties

Effect of nitrogen on the high temperature creep behavior of 9Cr-2Co steel

K.HARA et al.

Constant load creep tests were conducted at 873, 898 and 923 K under an initial stress of 50, 60 or 70 MPa to examine the effect of nitrogen addition (0.06, 0.11, 0.16 and 0.19 mass%) on the creep behavior of a 9mass%Cr-2mass%Co ferritic steel. Extraction residue analysis showed that 240 to 410 ppm of nitrogen was present as solid solution. The rest of the nitrogen existed as nitride precipitates. The creep rate decreased while creep rupture life increased with an increase in nitrogen content. It is also observed that the higher the nitrogen, the shorter the creep rupture strain. A state equation for creep could be represented as; $\dot{\varepsilon}_0 = A_0 \sigma_0^n \exp(-Q_0/RT)$, where $\dot{\varepsilon}_0$ is the imagi-nary initial strain rate defined in the text, A_0 is a constant, n is the stress exponent and Q_0 is the apparent activation energy. The mean values of n and Q_0 were 4.5 and 360 kJ/mol, respectively. The Orowan stress for specimens crept at 873 K and 70 MPa was estimated from the measurement of mean interparticle spacing obtained by TEM study. The resultant values are 15, 22, 30 and 38 MPa for specimens containing 0.06, 0.11, 0.16 and 0.19mass% nitrogen, respectively.

New Materials and New Processes

Reaction synthesis of TiC and Fe-TiC composites

M.J.CAPALDI et al.

The combustion synthesis of TiC and Fe-TiC by thermal explosion and self propagating high temperature synthesis has been investigated. The experimental methods are outlined and a method for the simultaneous measurement of wavefront velocity and maximum combustion temperature is described. The morphology of the products obtained is similar in both reaction modes. Values for the activation energy for each system were calculated and used to propose that the formation of Fe-TiC occurs *via* the formation of a $FeTi_2$ eutectic, liquid at the reaction temperature, which allows the transfer of carbon. In the TiC system the liquid phase is titanium.

Social Environmental Engineering

A trial to reproduce an ancient iron-making process in Chiba Prefecture (Review)

N.YAMAGUCHI et al.

A trial to reproduce an ancient iron-making process were carried out by the Boso-Fudoki-no-oka Museum. An object of the article is an introduction to operation data and the results of the trial. 7 times trials were carried out.

3.3kg of iron lump could be obtained by using 33kg of iron sand and 61kg of charcoal.