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## Fundamentals of High Temperature Processes

### Mechanisms of oxidation and vaporization of antimony from liquid copper with CuCl–CaO fluxes

*Y.CUI et al.*

In order to clarify the reaction mechanisms of oxidation and vaporization of Sb in liquid copper by using CuCl–CaO fluxes, the vaporization behavior from CuCl–$Sb_2O_3$ and CuCl–CaO–$Sb_2O_3$ fluxes and the reaction behavior of $Cu_2O$ between CuCl–$Cu_2O$ flux and liquid copper were observed at 1 423 K with argon gas.

For the vaporization from CuCl–$Sb_2O_3$ and CuCl–CaO–$Sb_2O_3$ fluxes, $SbCl_3$ and SbOCl in flux were observed in the fluxes, and these chloride and oxychloride vaporized to gas phase.

In the reaction between CuCl–$Cu_2O$ and liquid copper, the decomposition of $Cu_2O$ in the flux was confirmed, and the copper weight and oxygen content of copper increased.

The mechanisms of oxidation and vaporization of antimony in liquid copper by using CuCl–CaO fluxes were discussed based on the observed results. The $Cu_2O$ existing in CuCl–CaO flux is dissolved in copper melt, and the oxygen content of copper increases. The antimony in liquid copper is oxidized and removed to slag phase as $Sb^{3+}$. The formed $Sb^{3+}$ in flux vaporizes from flux as $SbCl_3$ and SbOCl.

(cf. *ISIJ Int.*, **48** (2008), 1)

### Development of a quasi-chemical viscosity model for fully liquid slags in the $Al_2O_3$–CaO–'FeO'–MgO–$SiO_2$ system. The experimental data for the 'FeO'–MgO–$SiO_2$, CaO–'FeO'–MgO–$SiO_2$ and $Al_2O_3$–CaO–'FeO'–MgO–$SiO_2$ systems at iron saturation

*A.KONDRATIEV et al.*

A structurally-based quasi-chemical viscosity model has been developed for the $Al_2O_3$–CaO–'FeO'–MgO–$SiO_2$ system. The model links the slag viscosity to the internal structure of melts through the concentrations of various anion/cation $Si_{0.5}O$, $Me^{n+}_{2/n}O$ and $Me^{n+}_{1/n}Si_{0.25}O$ viscous flow structural units. The concentrations of structural units are derived from the quasi-chemical thermodynamic model.

The focus of the present paper is the analysis of experimental data for fully liquid slags in the 'FeO'–MgO–$SiO_2$, CaO–'FeO'–MgO–$SiO_2$ and $Al_2O_3$–CaO–'FeO'–MgO–$SiO_2$ systems in equilibrium with metallic iron. Model parameters for the quasi-chemical viscosity model for the system $Al_2O_3$–CaO–'FeO'–MgO–$SiO_2$ are presented. The model has been optimised for the whole composition range at temperatures between 1 423 K and 1 873 K.

(cf. *ISIJ Int.*, **48** (2008), 7)

### Thermodynamic relation between aluminum and titanium in liquid iron

*W.-Y.KIM et al.*

Thermodynamic relation between aluminum and titanium in liquid iron was studied using the metal-nitride-gas equilibration technique. The effect of aluminum on the solubility product of TiN in liquid iron was measured under different nitrogen partial pressures in the temperature range of 1 843–1 973 K. The experimental results were thermodynamically analyzed using Wagner's interaction parameter formalism to determine the first-order interaction parameters of aluminum and titanium in liquid iron as follows.

$$e^{Al}_{Ti}=1\,939/T-1.009,\quad e^{Ti}_{Al}=1\,092/T-0.568$$

Using thermodynamic data determined in present study, a stability diagram for $Al_2O_3$, $Ti_2O_3$ and $Ti_3O_5$ phases was constructed as a function of dissolved aluminum, titanium and oxygen contents in liquid iron. The result indicated that at equilibrium condition titanium oxides would not form on titanium addition in Al-killed liquid steels with soluble aluminum content of 0.02–0.05 mass% at 1 873 K.

(cf. *ISIJ Int.*, **48** (2008), 17)

### Removal of antimony from liquid copper by using CuCl–$Na_2CO_3$ fluxes at 1 423 K

*Y.CUI et al.*

The removal rate of antimony from liquid copper by using CuCl–$Na_2CO_3$ fluxes was measured at 1 423 K with argon gas atmosphere. The addition of $Na_2CO_3$ to CuCl flux was relatively effective for the removal of antimony. The concentration of antimony in liquid copper largely decreased with time or with increasing $Na_2CO_3$ content in flux. About 99.8% of antimony was removed from liquid copper during 15 min. The metal weight and oxygen content of metal increased with time and with increasing $Na_2CO_3$ content in flux. These behaviors were mainly due to the decomposition of $Cu_2O$ formed in flux. The antimony in copper was oxidized.

According to the mass balance, about 60% of the removed antimony from liquid copper vaporized from the CuCl–23.8mass%$Na_2CO_3$ flux. The chlorination reaction between formed antimony oxide and CuCl might result in the vaporization of antimony from flux.

According to the above-mentioned experimental results, the CuCl–$Na_2CO_3$ fluxes were effective for the removal and recycling of antimony from liquid copper.

(cf. *ISIJ Int.*, **48** (2008), 23)

## Casting and Solidification

### Behavior of mixed grade during the grade transition for different conditions in the slab continuous casting

*M.ALIZADEH et al.*

In this study, the steel grade transition during the ladle change in a continuous casting process is simulated by presenting a new mathematical model. First, the mixing process in a non-isotherm tundish is investigated by a water modeling system. Then, heat transfer mechanisms and solidification process are simulated for a continuous casting machine and the geometric shape of the liquid pool is predicted considering different conditions. The mixing process in the liquid pool of strand is also investigated by a mixing model. Finally, when the solidification process in the strand is completed, the variations of chemical composition in the final product are calculated. To verify the results of the intermix model, several samples are taken from the different positions of the slab and chemical composition of several elements are measured using a spectrometry technique. The model results show that the weight of mixed grade steel are affected by parameters such as molten steel volume in the tundish at the time of new ladle opening, slab dimensions, rate of casting and non-isothermal effect on the tundish. The obtained results also show that the effect of mixing process on the extent of mixing regions in the liquid pool of strand is more significant than the mixing in the tundish.

(cf. *ISIJ Int.*, **48** (2008), 28)

### Re-start technology for reducing sticking-type breakout in thin slab caster

*C.-H.MOON et al.*

In order to increase the production rates and to secure the base production technology for the hard casting materials, a re-start casting technology as an active curing methodology has been developed to reduce the number of sticking type breakouts in the thin slab caster with high speed. It consists of the healing casting conditions of breakouts, the mold level control method for preventing the overflow or big change of molten steel near meniscus and the control of cooling rate at second cooling zone for rolling under the limits of rolling force and torque at the directly linked roughing mill. By applying the proposed technology, the automatic restarting rate of breakout is remarkably increased from 0 to 92%.

(cf. *ISIJ Int.*, **48** (2008), 48)

### Modeling of fluid flow and residence time distribution in a four-strand tundish for enhancing inclusion removal

*A.KUMAR et al.*

The introduction of the appropriate size and precise location of flow control devices such as dam, turbulence inhibitor, *etc.*, helps to modify the flow pattern and minimizing short circuiting and dead zone. Beside this, these also create the surface directed flow and maximize the residence time available for the flotation of inclusions and assimilation of the reaction products from the molten steel into the slag phase. These can be products of deoxidation, reoxidation, precipitation, emulsification and/or entrainment of refractory components into the melt and thus encompass both indigenous and exogenous inclusions. To this end, both the numerical and physical simulations were carried out mainly for three cases: a) in absence of flow control devices (*i.e.*, bare tundish), b) in the presence of a dam, and c) with the application of turbulence inhibiting device (TID) and dam combination in the existing tundish configuration. The commercial CFD (computational fluid dynamics) package FLUENT® was used to predict the flow field prevalent in the water model tundish at steady state, whereas in the experimental program, both Particle Image Velocimetry (PIV) techniques for flow measurements and tracer dispersion experiments for concentration measure-

ments were applied in the present study. Among all types of configurations applied in the present study, a combination of TID with holes+a dam work reasonably found to be an optimum configuration of the four-strand tundish regarding inclusion floatation. A superior strand similarity is also achieved in this configuration. Also the predicted time averaged horizontal and vertical components agreed within ±10% with the experimentally derived ones.

(cf. *ISIJ Int.*, **48** (2008), 38)

## Instrumentation, Control and System Engineering

### Hybrid modeling of molten steel temperature prediction in LF

*H. TIAN et al.*

Combining the conventional mechanism method with the newly developed intelligent algorithm, a hybrid model was developed for predicting the molten steel temperature in LF. The mechanism method is used to build the thermal model by analyzing the energy going into and out of the molten steel during the LF refining production process. It is hard to calculate the coefficients in the thermal model by mechanism method, so they are estimated by experience traditionally. In this paper, a new ensemble ELM algorithm using the modified AdaBoost. RT is proposed to calculate these coefficients. The new hybrid model overcomes the difficulty of obtaining the coefficients in thermal model, and solves the problem of limited prediction precision using "black box" model. The experiment demonstrates that the new hybrid model can improve generalization performance and the prediction accuracy.

(cf. *ISIJ Int.*, **48** (2008), 58)

## Forming Processing and Thermomechanical Treatment

### The deformation and the redundant work factor in the axisymmetric drawing of AISI 420 stainless steel bars—Strain path effects analysis

*E.C.S. CORRÊA et al.*

In the present work, experimental techniques for evaluating the deformation and the redundant work factor in the axisymmetric drawing of ferritic AISI 420 stainless steel bars were investigated. Six operation conditions, involving two reductions of area and three die semi-angles, were employed in the study. Regarding the redundant deformation analysis, the visioplasticity technique was considered as the most adequate procedure for estimating the average deformation in drawing. In this case, an increasing relationship between the redundant deformation factor and the parameter $\Delta$ was obtained. On the other hand, the stress–strain curves superposition technique led to redundant deformation factor values almost insensitive to variations of the parameter $\Delta$ and below unity, a phenomenon which was associated with strain path effects. Concerning the redundant work factor study, the experimental results were lower than those obtained through a theoretical approach and, in some conditions, below unity. This was also attributed to strain path effects.

(cf. *ISIJ Int.*, **48** (2008), 63)

## Welding and Joining

### Characteristics of microstructure in ultrahigh carbon steel produced during friction stir welding

*Y.S. SATO et al.*

Ultrahigh carbon steels containing 1 to 2 wt% C have very poor fusion-weldability, but exhibit high strength-ductility balance, good wear resistance and superplasticity at high temperatures, when a microduplex structure consisting of a fine ferrite grain structure with a uniform distribution of spheroidized cementite is formed. Thus, ultrahigh carbon steels with the microduplex structure show promise for use in construction. In the present study, two kinds of initial microstructure, a fully pearlitic structure and a microduplex structure, were produced in an ultrahigh carbon steel with 1 wt% C by different thermal treatments, this steel then being subjected to friction stir welding (FSW) at different rotational speeds using a polycrystalline cubic boron nitride tool. The feasibility of friction stir welding for ultrahigh carbon steel and the effect of welding parameters and initial microstructure on the residual microstructure characteristics of the weld were systematically examined. FSW successfully yielded defect-free welds in the ultrahigh carbon steel at all welding parameters employed. All welds exhibited very high hardness in the weld center due to the martensitic transformation. The difference in characteristics of the martensitic structure among the welds was negligible, but the austenite substructure was affected by the rotational speed. Microstructural development of various regions in the welds was reasonably accounted for by the friction stir welding process, the thermal stability of the initial microstructure and the solid-state transformation during cooling cycle of FSW.

(cf. *ISIJ Int.*, **48** (2008), 71)

### Hot cracking of resistance spot welded magnesium alloy

*B. LANG et al.*

Crack features of resistance spot welded magnesium alloy joint and effects of welding parameters on susceptibility of the joint to hot cracking have been investigated. In the spot welded joints, solidification cracking in weld nugget and liquation cracking in heat-affected zone (HAZ) were often observed. The formation of solidification cracking is related to low melting point liquid films between dendrites due to segregation of Al and Mn atoms and tensile stress developed during cooling. In HAZ, the grain boundary melting occurred and grain became coarser. The liquation cracking appears in HAZ just adjacent to weld nugget and may be induced by solidification cracking at the edge of weld nugget. The welding parameters (heat input) have an obvious effect on susceptibility of weld nugget to hot cracking. The results show that relatively high heat input (*i.e.* relatively high welding current, long welding time or low electrode force) increase the hot cracking tendency. It is favorable to select relatively low heat input for reducing susceptibility of spot welded magnesium alloy joint to hot cracking.

(cf. *ISIJ Int.*, **48** (2008), 77)

## Surface Treatment and Corrosion

### IS evaluation of chromate and organic coating layers on corrosion performance of galvanized steel sheets

*K. RAEISSI et al.*

EIS results show that corrosion resistance of chromate zinc is mainly due to its passivity behavior. This passivity was not enough to prevent chromate zinc from corrosion in NaCl solution, but in hard and soft waters, it prevented zinc corrosion favorably. This different behavior was attributed to adsorption of a chromate ion associated complex in hard and soft waters. Results showed that chromate zinc behaves more favorably in hard water than soft water by increasing the immersion time. This was related to the increased tendency of the complex adsorption at long times of immersion. The complex adsorption was not occurred in distilled water resulted zinc corrosion. A primer layer applied on chromate zinc acts as a barrier and then electrolyte solution can reach the chromate layer only through the coating pores. In this way, electrical double layer could be build up locally at bottom of the pores. Therefore, high corrosion resistance is expected to achieve only if the chromate zinc can reach to the passivity state at the bottom of the pores. A primer/topcoat layer due to its extremely high pore resistance can prevent zinc corrosion in NaCl solution even after eight weeks exposure.

(cf. *ISIJ Int.*, **48** (2008), 83)

### Evaluation of sliding wear resistant property of C.P. titanium and SP-700 titanium alloy surface-hardened by Ar–5%CO gas

*Y.Z. KIM et al.*

Sliding wear resistant properties of C.P. titanium and SP-700 alloy surface-hardened by Ar–5%CO gas were evaluated using a counterpart material of a bearing steel, JIS SUJ-2 steel and Nishihara type of sliding wear testing machine. In the latter, two disk specimens were rotated at different rotating speeds under a given compressive applied load, yielding a sliding ratio of 20%. Wear tests were repeated intermittently for several times, and a respective test time period in each series of wear tests was primarily varied. The mass loss in both disks was measured after each test. Wear resistance of annealed C.P. titanium without surface hardening was inferior to that of annealed SUJ-2 steel, but surface hardened C.P. titanium resulted in superior wear resistance over quench-tempered SUJ-2 steel with a hardness of 720 in Hv. Observation results of worn surfaces in both disks indicate that preferential wear occurred in the convex region of a furrow-like pattern formed by a lathe machining, resulting in a reduction of surface roughness values with wear progress. When a respective test time period was extended to 21.6 ks, adhesive wear took place between worn surfaces in both specimens, and the mass loss ratio in titanium

disk increased at a much higher rate compared with that of a respective test time period of less than 14.4 ks. The steel debris torn off from worn surface of SUJ-2 steel disk was observed to adhere to the worn surface in surface hardened C.P. titanium disk. Wear resistant property of surface hardened SP-700 alloy was also superior to quench-tempered SUJ-2 steel.

(cf. *ISIJ Int.*, **48** (2008), 89)

## Transformations and Microstructures

### Effects of Nb and C in solution and in NbC form on the transformation-related internal friction of Fe–17Mn (mass%) alloys

*T. SAWAGUCHI et al.*

The effects of presence of Nb and C in solution or in the form of NbC precipitates on the transformation of binary Fe–17mass%Mn alloys were evaluated from micro structural and macroscopic point of view. At microstructural level precipitation of NbC was accompanied by the decrease of both relative amount of $\varepsilon$ martensite and martensite plate thickness. The precipitation was associated with a general increase of proof stress and thermal hysteresis on the internal friction curves as well as a decrease of the maximum value of internal friction, caused by martensitic transformations, as evaluated by means of a dynamic mechanical analyzer. The solute atoms slightly reduced internal friction and the NbC precipitates markedly reduced internal friction, probably due to the pinning effect on the oscillated motion of Shockley partial dislocations.

(cf. *ISIJ Int.*, **48** (2008), 99)

### Analysis of copper effect on microstructures and mechanical properties in microalloyed steels

*A.M.ELWAZRI et al.*

The microstructure and mechanical properties under cool deformation conditions was investigated for three steels of approximately 0.03 % carbon with different alloying additions of niobium and copper. Compression testing of the three steels was employed to study the influence of processing conditions (cool deformation) and chemical composition (niobium and copper) on the microstructure and mechanical properties. Overall, for the steel compositions examined, the addition of copper increased the strength. This can be explained by solid solution hardening effect of copper. The results show that there is very fine equiaxed ferrite that has formed, either by recrystallization or transformation induced by cool deformation.

(cf. *ISIJ Int.*, **48** (2008), 107)

## Mechanical Properties

### The effect of Co–N addition on mechanical properties, microstructure and erosion of 17Cr steels

*J.-W.LEE et al.*

The effect of Co–N addition on mechanical properties, microstructure and water-jet erosion of heat-treated 17Cr steels was examined focusing on hardness, grain size, phase volume fraction and erosion damage. In the heat-treatment temperature range, the hardness and strength of Co–N added 17Cr steels are somewhat higher than those of non-added 17Cr steel. In the 950 to 1 100°C quenching temperature range, grain size, hardness and volume fraction of retained $\gamma$ and $\delta$-ferrite increased with increasing quenching temperature. The grain size in Co–N added 17Cr steels was finer than that in non-added 17Cr steel and the volume fraction of retained $\gamma$ and $\delta$-ferrite in Co–N added 17Cr steels was smaller than that in non-added 17Cr steel. The Co and N content measured by EDAX and Auger analysis were mostly contained in the matrix; therefore, Co–N added 17Cr steels probably contributed to solid solution strengthening and restraint of $\delta$-ferrite formation in the matrix. Under the tempering treated conditions, hardness patterns are divided into three regions (maximum softening region in 250 to 350°C, secondary hardening and temper brittleness region in 400 to 500°C, maximum softening and precipitation region in 550 to 700°C). All of the Co–N added and non-added 17Cr steels had similar hardness patterns when plotted against tempering temperatures; however erosion damage depth of the Co–N added 17Cr steels in high-pressure water-jet tests was somewhat less than that in Co–N non-added 17Cr steel.

(cf. *ISIJ Int.*, **48** (2008), 114)