Necessity of scrap reclamation technologies and present conditions of technical development (Review)

K.NORO et al.

"New Steelmaking Process Forum" was inaugurated in 1991 for the purpose of developing an innovative process capable of contributing to global environmental protection, such as the effective utilization of iron resource and the reduction of carbon dioxide generation, by recycling the total volume of scrap. This paper outlines the Forum's activities.

The contents of tramp elements, copper and tin, of waste scrap were predicted to increase to 1.5 times and 1.2 times the present values in 2010. Even if the largest possible amount of waste scrap is recycled within the allowable ranges of steel product composition values, 150-300 million tons of waste scrap will be heaped up in Japan. Therefore, copper and tin removal technologies were developed. For the mass impurity (copper), the technology to crush scrap at low temperature at the time of pretreatment and the technology to automatically discriminate and separate impurity-attached scrap were developed. For the surface layer impurity (tin), the technology to remove it by oxidation in a high-temperature oxidizing atmosphere at the time of preheating and melting and the technology to remove it by evaporation in a weakly oxidizing atmosphere were developed. For zinc, the technology to remove it from dust in an externally heated kiln was developed.

Hot Shortness and Ductility

Solid/liquid equilibria in Fe-Cu based ternary systems

H.OHTANI et al.

The effect of alloying elements on the solubility of Cu in solid Fe has been investigated by using solid-liquid diffusion couples. An addition of Co, Ni, and Al results in an increase of the solubility of Cu, while that of V, Cr, Mn, Si, and Sn decreases the solubility. Thermodynamic calculation of the solid/liquid phase equilibria in the Fe-Cu-X ternary system has been also performed, where a set of thermodynamic parameters of solid and liquid phases has been evaluated. Furthermore, the equation that describes the change of the solubility of Cu in solid Fe with an addition of alloying elements has been derived by thermodynamic analysis of these experimental values.

Effect of Cu, Sn and Ni on hot workability of hot-rolled mild steel

N.IMAI et al.

The effect of tramp elements Cu and Sn on the hot workability of mild steels was investigated in this paper. A hot rolling condition was simulated by oxidizing followed by tensile-deforming and the hot workability was assessed by measuring the number of surface cracks. The microstructure at the scale/steel interface was closely observed, and the relationship between the surface cracking and the microstructure was established.

Sn as low as 0.04% increased the number of cracks in an 0.3% Cu bearing steel, while 0.3% Ni suppressed the cracking in an 0.3% Cu-0.04% Sn bearing steel. An energy dispersive X-ray spectroscopy (EDX) at the subscale layer of the oxidized Cu-Sn bearing steel revealed that an 82% Cu-7% Sn-Fe alloy phase formed at the scale/steel interface. The phase calculation using the Thermo-Calc computer program showed that Sn decreased the solubility limit for Cu in Fe, thus increasing the amount of liquid Cu enriched alloy and enhancing the surface cracking by Cu liquid embrittlement.

On the other hand, an addition of 0.3% Ni to the 0.3% Cu-0.04% Sn bearing steel formed two different Cu-Sn phases at the surface of the steel; a 12% Cu-19% Ni-Fe layer under the steel surface and a liquid 63% Cu-12% Sn-12% Ni-Fe alloy placed above the layer. The amount of the 63% Cu-Sn-Ni-Fe alloy was a little, and the 12% Cu-Ni-Fe layer was in a large amount. In addition, the phase calculation at an oxidation temperature 1 100°C showed that the Cu and Ni enriched layer was solid. Therefore, the addition of 0.3% Ni suppressed the surface cracking in the Cu-Sn bearing steel. A mechanism of the reduced amount of liquid by increasing Ni content was discussed in terms of local equilibrium and inward diffusion of Cu atoms from the Cu enriched layer into the steel.

Effect of Cu and Ni on hot workability of hot-rolled mild steel

N.IMAI et al.

The effect of a tramp element Cu on the hot workability of steels was investigated in this paper. The number of surface cracks occurring in the specimens which are tensile-deformed after oxidized was measured to assess the effect of small amounts of Cu(0.3%) and Ni(0.15%) on hot workability. The microstructure of a scale/steel interface was closely observed and the relationship between the surface cracking and the microstructure was established.

For an 0.3% Cu bearing steel, the surface hot cracking occurred only at 1 100°C oxidation due to a liquid Cu enriched phase, *i.e.*, 87% Cu-Fe, formed at the scale/steel interface. Both at 1 000°C and at 1 200°C oxidations, solid Cu enriched phases formed at the steel interface, which did not cause surface cracking. A liquid Cu enriched phase in a small amount was occluded into the scale at 1 200°C. An addition of 0.15% Ni suppressed the surface cracking of 0.3% Cu bearing steel by eliminating all the Cu enriched liquid phases. At 1 100°C oxidation, Ni addition enhanced the occlusion of a solid Cu enriched phase, *i.e.*, 66% Cu-15% Ni-Fe, and left a solid phase, 16% Cu-16% Ni-Fe, at the scale/steel interface. At 1 200°C oxidation, Ni addition also enhanced the occlusion of solid phases, 16% Cu-27% Ni-Fe and 10% Cu-10% Ni-Fe, and left a solid phase, 6% Cu-1% Ni-Fe at the interface. A mechanism of formation of various Cu-Ni enriched phases in 0.3% Cu-0.15% Ni bearing steel was discussed in terms of equilibrium diagrams and the difference in diffusion rate of Cu and Ni.

Evaluation of susceptibility to surface hot shortness in Cu-containing steels by tensile test

S.-J.SEO et al.

The feasibility of a new method for evaluating the susceptibility of steels to surface hot shortness due to Cu and Sn was examined. Steels used are IF steels containing 0.1～0.2% Cu and 0.1% C-0.4% Cu steels. Chemical compositions of the IF steels were controlled with the purpose of being as similar as possible to those of steels of which the susceptibility was previously examined by a visual method in a practical rolling process at Nippon Steel Corporation. Tensile tests were carried out at 1 100°C after heating a specimen in air or Ar gas. The total elongation and maximum load were measured from a load-elongation curve. By dividing the difference between the total elongations or maximum loads obtained in air and Ar gas by the total elongation or maximum load in Ar gas, the parameters Ee or Ep were calculated. By considering the reduction in specimen diameter due to oxidation, the Ep corrected, Ep', was calculated. The Ee, Ep and Ep' of the IF steels corresponded to the degree of the penetration of surface cracks observed in the practical rolling process. Penetration of Cu-enriched phase into grain boundaries tends to occur under thermal and external stresses. Surface cracks stop growing along the depth direction at the earlier stage of deformation when the amount of Cu-enriched phase is the smaller at steel/scale interface. Tensile tests using specimens having artificial round cracks clarified that the Ee and Ep' increased with an increase in the crack depth and that, in contrast, the Ep' increased slightly and the Ee decreased with an increase in the number of cracks. The parameter Ee and Ep' showed a maximum value at a strain rate of around $3\times10^{-2}s^{-1}$, and the difference in their values among the steels is largest around this strain rate. Therefore it is possible to know sensitively the effects of any factors like alloying or impurity elements on surface hot, shortness at around this strain rate although this strain rate is much slower than those of hot workings.

Effect of 0.4%Si and 0.02%P additions on surface hot shortness in 0.1%C-0.5%Mn steels containing 0.5%Cu

S.-J.SEO et al.

The objective of this paper is to examine the effects of Si and P in low carbon steels on surface hot shortness due to Cu. Susceptibility of the steels to surface hot shortness was evaluated by a new method using tensile tests which is proposed by the present authors. Tensile tests were carried out after heating specimens at 1 000, 1 100 and 1 200°C in air and in Ar gas. Tensile tests using specimens implanting a Cu rod, observation of oxidation rate by thermogravimetry, optical microscopy and EPMA of steel/scale interface region *etc.* were also performed. At 1 100°C, single additions of 0.4% Si and 0.02% P were effective to decrease susceptibility to surface hot shortness, however these increased the oxidation rate. Duplex addition of 0.4% Si and 0.02% P decreased the oxidation rate and exhibited a substantial effect on a decrease in the susceptibility. Addition of Si decreased the amount of Cu-enriched phase at steel/scale interface. This is contributable to the reduction of the susceptibility to surface hot shortness. Internal oxidation of Si is thought to decrease the amount of the Cu-enriched phase. Single addition of 0.02% P seems to increase slightly the amount of the Cu-enriched phase. A critical stress exists to fracture the specimens by Cu-enriched liquid phase. The additions of Si and P increase this critical stress. Silicon also contributes to a decrease in the growth rate of the crack created by the penetration. At 1 200 °C, the susceptibility to surface hot shortness in all steels decreased compared with that at 1 100°C, but trends of effects of single and duplex additions of 0.4% Si and 0.02% P on the susceptibility were similar to those at 1 100°C. The oxidation rate for all steels was much higher than at 1 100°C, but the amount of Cu-enriched phase at steel/scale interface was reduced compared with at 1 100°C. The amount of the Cu-enriched phase in the steels containing 0.4% Si is smaller than that in other steels. Liquid phase which appears in scale at temperatures higher than 1 177°C (eutectic temperature of $FeO\text{-}2FeO\cdot SiO_2$) is a contributing factor in both increases of the oxidation rate and occlusion of Cu into the scale at 1 200°C.

Strain rate dependence of Cu embrittlement in steels

H.G.Suzuki

The strain rate dependence of liquid Cu embrittlement was studied by a simulated hot tensile test. Carbon steel containing 0.1% C showed this embrittlement at 1 323K, just below the melting point of pure Cu. Fe-36Ni showed a very distinct embrittlement in the temperature range between 1 350 and 1 473K. This embrittlement strongly depends on the strain rate in both 0.1C steel and 36Ni alloy. Faster strain rate than the velocity of grain boundary penetration of liquid Cu improves hot ductility and shows no embrittlement. CP Ti does not show any embrittlement.

Influence of Cu and Sn on hot ductility of steels with various C content

H.Matsuoka et al.

The influence of Cu and Sn on the hot ductility at the strain rate of 10^{-3} s^{-1} for steels with C contents from 0.002 to 0.15 mass% was investigated. The hot ductility dropped at austenite + ferrite two phase region just below A_3,namely, 800 to 900°C. The hot ductility deteriorated more at higher C content, and furthermore with the co-addition of Cu and/or Sn. It was considered that the deterioration at austenite + ferrite two phase region in the Cu, Sn bearing steel was caused by the combined effect of follwing factors : (1) the formation of proeutectoid ferrite along the austenite grain boundaries, (2) the segregation of Sn at the interface between proeutectoid ferrite and austenite or at the austenite grain boundaries, and (3) the increase in the difference of the deformation strength between austenite and proeutectoid ferrite.

Scale Properties

Failure of scales formed on Cu-containing low carbon steels during cooling

S. Taniguchi et al.

Low carbon steels containing 0 to 1.5 mass% Cu were oxidised in air at 1 073, 1 150, 1 273 and 1 386K for up to 3.6 ks. An acoustic emission (AE) technique was used to assess the temperature at which mechanical failure of the scale takes place during cooling in static air. The conventional metallographic examinations revealed that the scales consist mainly of two FeO layers ; the inner layer is porous FeO and the outer layer is dense FeO for oxidation temperatures of up to 1 273K. Cu and Si are enriched in the porous FeO layer at the interface of the two FeO layers. At 1 386K an FeO layer containing Fe_2SiO_4 (fayalite) grains is formed instead of the inner porous FeO layer. Cu is enriched at the scale/substrate interface, while Si is enriched as Fe_2SiO_4 grains in the inner FeO layer near the both interfaces. The enrichment of Cu is unrecognisable for the Cu content less than 0.5%. The modes of scale failure observed are (a) partial separation at the two FeO layers, (b) partial separation at the scale/substrate interface, (c) through-scale crack almost normal to the substrate surface, (d) shear crack in the inner FeO layer at about 45 degrees to the substrate surface and (e) blistering of a thin Fe_2O_3 layer over a small area. The frequency is in this order ; *i.e.* (a) is most frequently observed and (e) is very rare. The values of ΔT (oxidation temperature-failure temperature) detected by the AE measurement were converted into the apparent thermal stresses to cause the scale failure. The stress increases in a range 0.5 to 1 GPa as the oxidation temperature rises up to 1 273K. A further temperature rise slightly decreased the stress. This is attributable to the formation of Fe_2SiO_4 grains in the FeO layer. The increase in the Cu content slightly increases the stress.

Influence of Ni Impurity in steel on the removability of primary scale in hydraulic descaling

T.Asai et al.

Influences of Ni impurity on the removability of primary scale in hydraulic descaling were investigated in 0.02 and 0.1 mass% Si mild steels. And the thickness distribution of residual scale was discussed in relation to the unevenness of the scale/steel interface. The removability of primary scale reduced due to the existence of Ni impurity ranging to 0.05 mass% in each steel. With an increase in Si content up to 0.1 mass%, the removability of Ni added steels showed heating temperature dependence between 1 150 and 1 250°C. The existence of Ni impurity made the scale/steel interface of steel uneven. Estimating the unevenness of the interface by measuring the interface length, it was found that the austenite transgranular unevenness governs the change in the total interface length rather than the oxide invasion into austenite grain boundaries.

A reduction of scale removability caused by Ni impurity was explained by the increased interface length. In spite of the large differ ence in scale removability between 0.02 and 0.1 mass% Si steels containing more than 0.05 mass% Ni, the unevenness of the scale/steel interface was the identical with each other. Therefore, the temperature dependence of the scale removability in Ni added 0.1 mass% Si steel was not explained by this factor. Other mechanisms concerning fayalite formation and its morphology should be taken into account for this behavior.

Surface Science and Technology

In situ observation of preferential anodic dissolution of phosphorus compound in Fe-P alloys using Raman spectroscopy

H.Tanabe et al.

The solution chemistry of P in the Fe-P alloy electrodes containing P of 0.104, 0.028, and 0. 004 mass% has been investigated by using *in situ* Raman spectroscopy in an electrochemical cell under controlled potential in 0.1 $kmol\cdot m^{-3}$ NaOH at 25°C. It is found that the segregation site of the precipitate with the chemical composition of F_3P dissolves preferentially. Using *in situ* Raman spectroscopy three dissolution species of PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ were detected on the surface at the segregation site, and these concentrations depend on the location of the precipitate of P compound whether at grain boundary or in grain. The detection of HPO_4^{2-} and $H_2PO_4^-$ both of which are unstable in the solution of NaOH suggests that the localized corrosion at the segregation site of P induces decrease of pH.

Influences of Cu in steel on the formation of alloy layer in hot-dip galvanizing

A. KOMATSU et al.

The influence of Cu in steel on hot-dip galvanizing of hot rolled steel was studied. We investigated the formation of the alloy layer formed at the overlay-substrate interface. On Cu-Ti-added steel, the formation of δ_1 phase was promoted. while Fe_2Al_5 was the main phase on the usual Ti-added steel. We concluded that this phenomenon was caused by the dissolution of Cu into the Zn bath that had deposited on the surface during pickling, and suggested that the dissolution of Cu should decrease the activity of Al and make Fe_2Al_5 less stable than that of Ti-added steel, which caused the easy precipitation of δ_1.

Phase Transformation and Microstructure

Phase transformation mechanism of Fe-Cu alloys

Y. KIMURA et al.

Fe-(0.5~4)mass% Cu alloys were cooled from γ field under various cooling conditions (water-quenching, air-cooling, furnace-cooling) and phase transformation mechanisms were investigated by means of microstructural examinations and dilatometry.

In all of the cooling conditions, hardness of Fe-Cu alloys becomes higher with increasing Cu content. Effect of cooling conditions on hardness tends to be significant in alloys with Cu more than 1 mass%. TEM observation shows that strength of alloys depends not only on a difference of matrix ; martensite or ferrite, but also on dispersion of ε-Cu particles. In the case of air-cooling for an Fe-4mass% Cu alloy, the alloy undergoes preferentially $\gamma \rightarrow \alpha$ massive transformation and then ε-Cu particles precipitates finely within the massive ferrite matrix. This leads to a large strengthening with a moderate ductility. Strength of Cu bearing steels can easily be controlled by varying cooling condition after a solution-treatment: Steels are soft enough to be deformed and machined after furnace-cooling, but strengthened after resolution-treatment followed by air-cooling.

Effects of Cu on diffusional transformation behavior and microstructure in Fe-Mn-Si-C steels

H. OHTSUKA et al.

The amount of scrap has been increasing in recent years and the recycle of scrap has become a very important issue in point of preserving ecological environment. Actually the quality of scrap has been declining these days due to the increasing concentration of tramp elements, which mean the impurities such as Cu, Sn, As, Sb, Cr, Ni, *etc*, that are hard to be removed from the steel and accumulated in scrap during steel making process. Therefore it is necessary to make use of the scrap by taking into account the effect of tramp elements on the quality of steels. In this study, Cu was picked up as a target element and effects of Cu addition on the isothermal transformation behavior and the transformed structure have been investigated in Fe-1.48Mn-0.48Si-0.15C-(0, 1.51)Cu (wt%) steels. The main results are ; (1) The transformation behavior is retarded by the addition of Cu in the temperature range of 873 to 973K. (2) The isothermally transformed structure at 903K is mainly acicular ferrite in 0Cu steel, but is equiaxed ferrite with lots of subgrains in 1.5Cu steel. (3) Both the nucleation rate and growth rate of ferrite are decreased by the addition of Cu and this is considered to be caused by the reduction in austenite grain boundary energy due to segregation of Cu and the solute drag effect by Cu.