Promotion of recycling of steel through suppression of surface hot shortness due to copper by physical metallurgy

Koji SHIBATA

Department of Metallurgy, The University of Tokyo, 1-3-7 Hongo, Bunkyo-ku Tokyo, 113-8685 Japan
 TEL:x81-3-5841-7147 FAX:x81-3-5841-7147 e-mail:kshibata@steel.mm.t.u-tokyo.ac.jp

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The most serious problem in recycling of steel is surface hot shortness during hot deformation due to Cu mixed from scrap into steels. Tin accelerates the effect of Cu. Several methods have been researched to suppress this shortness. However, it is difficult to separate Cu and Sn from steel scrap using physical and chemical methods and to remove these elements from steels by current smelting process. Therefore, Cu and Sn accumulate in steels produced using steel scrap: such elements are called tramp elements. On the other hand, Cu has a potential to increase strengths and corrosion resistance of steels, which might decrease environmental load during the life cycle of steels. The surface hot shortness occurs through preferential oxidation of Fe atoms during heating for hot deformation and formation of liquid Cu-enriched phase at the steel/scale interface. Therefore, there exist tolerable contents of Cu and Sn in commercial steels. The amount of Cu in steel scrap is increasing in Japan year by year. Therefore, in the present research, the details of the mechanism of the surface hot shortness are examined in order to find the ways for the suppression of the shortness by controlling microstructures near the steel/scale interface through physical metallurgy. Controlling of microstructures can be performed by the optimization of contents of harmless alloying and impurity elements, heating temperature, heating atmosphere and deformation rate.

Keywords : Tramp element, Oxidation, Liquid embrittlement, Scale, Occlusion, Control of micro-structure, Heating temperature, Heating atmosphere, Deformation rate, Grain size

I. INTRODDUCTION

Amount of steel accumulation in Japan is steadily increasing year by year. As a natural result, the amount of steel scrap, especially obsolete steel scrap, is expected to increase at a considerable rate as reported by JRCM (the Japan Research and Development Center for Metals).¹ Therefore the usage of steel scrap has become important in steel making in Japan from the viewpoints of saving of resources and restraining of environmental problems.

In addition, the quality of the steel scrap is decreasing. That is to say, concentrations of Cu and Sn, especially Cu, in steel scrap are also increasing. Copper is mainly contained in the scrap of cars and home electronic appliances. Tin is mainly in the scrap of tin-coating can. Once these elements are mixed into steels it is difficult to remove them

from steels in the current steel smelting process. So they travel around steels and scrap and accumulate in steels. Therefore, they are called tramp elements.

Copper increases generally strengths and corrosion resistance of steels and may decrease environmental load during the life cycle of steels. Copper, however, causes a serious problem in the mechanical working like hot rolling and limits the usage of steel scrap. That is to say, Cu tends to be enriched at the steel/scale interface by selective oxidation of Fe atoms. Copper-enriched phase liquefies during the heating for hot working and penetrates into austenite grain boundaries under the stress during hot rolling or forging processes to cause cracks on the steel surface. This phenomenon is well known as surface hot shortness due to copper. Tin accelerates this hot shortness.² Therefore, there exist

Table 1. Ways for suppression of surface hot shortness due to Cu.

① reducing Cu in iron scrap by design of fabrication
② reducing Cu in iron scrap by separation
③ reducing Cu in steel by smelting
④ suppressing the shortness by physical metallurgy

tolerable contents of Cu and Sn in commercial steels. However, steel scrap containing these elements more than the tolerable values is growing in the amount.

There are several ways for suppression of the surface hot shortness as shown in Table 1. It seems, however, impossible for the way ① to be feasible in several years. As for the ways ② and ③, recently in Japan, large efforts have been made to separate Cu and Sn from steel scrap and steels.¹ But it has been clarified that they are not easy. Therefore the grope of the present author has insisted the necessity of the suppression by physical metallurgy, the way ④.³⁻⁷ The way ④ aims to suppress the surface hot shortness through controlling microstructures around the steel/scale interface in order to reduce the volume of Cu-enriched phase penetrating into grain boundaries. The volume of liquid Cu-enriched phase penetrating into grain boundaries can be reduced by the suppression of oxidation, the occlusion of the phase into scale, back-diffusion of the phase into steel, suppression of wettability or fluidity of the phase and so on. These were performed in the present research by optimization of contents of harmless alloying and impurity elements, heating temperature, heating atmosphere and deformation rate.

Nickel increases the solubility of Cu in steel and the melting point of Cu-enriched phase. Therefore addition of nickel is effective to suppress the surface hot shortness. Removal of nickel in the current smelting process, however, is difficult. In addition nickel is expensive. So, other ways for the suppression of the shortness are desired.

Table 2 shows the present tolerable concentration of Cu and Sn in some representing steels and the target of our research.

Table 2. Present tolerable amount of Cu and Sn in some steels and the targets of our research (mass%).

Steels		Cu	Su
sheet	(drawing)	0.06→0.2	0.01→0.03
sheet	(commercial)	0.10→0.3	0.02→0.04
	shape	0.30→0.4	0.03→0.05
	bar	0.40→0.5	0.06→0.08

In the present paper the feasibility of the way for the suppression of the surface hot shortness using physical metallurgy will be mentioned.

II. EXPERIMENTAL PROCEDURES

II-A. Steels

Many steels were melted in vacuum furnaces and effects of P, Si, Mn, S, C, Ni, Sn, Al and B were investigated. Copper contents (mass%) in these steels were mainly 0.5% and 0.2% Cu steels were also partially examined. For instance, Table 3 shows the chemical composition of the steels melted in order to know effects of a very low content of boron.

II-B. Tensile tests at elevated temperature and evaluation of susceptibility to the surface hot shortness

Round bar specimens were machined from hot rolled plates. Tensile tests were carried out mainly at the strain rate of $2.8 \times 10^{-2} \text{ s}^{-1}$ after heating the specimen at 1100°C or 1200°C for 30 min in oxidizing atmospheres. Similar tensile tests were also performed after heating in Ar gas. Susceptibility to the surface hot shortness was evaluated using values of the parameters calculated from the maximum load and total elongation. Two kinds of oxidizing atmospheres were used : air and a controlled atmosphere of 74%N₂-16%H₂O-8%CO₂-2%O₂ of which composition is similar to that of the combustion gas of LNG practically used in heating furnaces.

Table 3. Chemical composition of the steels used to know the effects of boron (mass%).

Steels	C	Si	Mn	P	S	Cu	Ni	Cr	Al	Ti	B	N	O
A	0.100	<0.01	0.50	0.001	0.002	0.48	<0.01	<0.01	0.037	0.041	<1	13	20
B	0.100	<0.01	0.51	0.001	0.001	0.48	<0.01	<0.01	0.051	0.041	7	9	20
C	0.099	<0.01	0.51	0.001	0.001	0.49	<0.01	<0.01	0.053	0.042	28	11	20
D	0.098	<0.01	0.51	0.001	0.001	0.48	<0.01	<0.01	0.053	0.042	48	14	20

The parameters were calculated by the following equations:

$$Ep(\%) = (P_{Ar} - P) / P_{Ar} \times 100$$

$$Ep'(\%) = (P_{Ar} - P') / P_{Ar} \times 100$$

$$Ee(\%) = (\delta_{Ar} - \delta) / \delta_{Ar} \times 100$$

where P_{Ar} and P are the maximum load in Ar gas and in oxidizing atmospheres, respectively. P' is corrected value of the maximum load considering the reduction in the diameter of specimens by oxidation. δ_{Ar} and δ are total elongation in Ar gas and in oxidizing atmospheres, respectively.

Our previous research³ showed these parameters represent the susceptibility to the surface hot shortness very well. These parameters show the larger values as the maximum depth of surface cracks increases.

II-C. Observation of oxidation rate by thermo-gravimetry

A weight increase by oxidation of the steel was measured using a thermo-balance in air and in the LNG combustion gas during heating at 20°C/min and holding at 1100°C for 30min. The geometry of the specimen was a cylinder of 5mm diameter and 3mm height.

II-D. Optical microscopy

Specimens of 10×10×10mm were heated in air and in the LNG combustion gas and then air cooled. They were mounted in epoxy resin and polished mechanically to be subjected to optical microscopy.

II-E. Tensile tests using specimens implanted a Cu or Cu alloy rod

In order to examine effects of certain elements in steels or Cu-enriched phase on the penetration of liquid Cu-enriched phase into grain boundaries, tensile tests were carried in Ar gas after heated at 1100°C for 30 min using specimens implanting a rod of tough-pitch Cu or Cu alloy.⁴⁻⁸

III. RESULTS AND DISCUSSION

III-A. Effects on values of Ep, Ep' and Ee

It has been clarified that addition of Si, P, Mn, S (+Mn), C and B reduce the susceptibility to the surface hot shortness. Therefore, it is recommended to alloy these elements up to the acceptable contents considering other properties.

In Fig.1 the effects of boron on Ep, and Ep' of the steels shown in Table 3 are exhibited. Addition of 7ppm B decreases the susceptibility for the surface hot shortness. But the effect reduces by further addition of boron.

III-B. Effects on oxidation rate

The susceptibility to the surface hot shortness can

be scarcely explained by the effects of elements on oxidation rate.⁴⁻⁸

III-C. Effects on microstructure

By optical microscopy it was clarified that Si, Mn, S(+Mn) and B reduce the volume of Cu-enriched

Fig.1 Effects of boron on Ep, and Ep' of the steels shown in Table 3.

phase at steel/scale interface. Remarkable occlusion of Cu-enriched phase into scale was observed in Si added steels.

Figure 2 shows effects of boron on microstructure at steel/scale interface of the steels shown in Table3 heated at 1100°C in the LNG combustion gas. Volume of Cu-enriched phase seems to be reduced a little by the addition of 7ppm boron. Further addition of boron enhanced grain boundary oxidation.

III-D. Effects on penetration of liquid Cu into austenite grain boundaries

Phosphorous, Si and B restrain the penetration of Cu-enriched phase into austenite grain boundaries. Figure 3 shows the effect of B on the penetration. As the content of B increases, the penetration is suppressed. Using alpha particle track etching method (autoradiography using B¹⁰), segregation of B along austenite grain boundaries was observed. Therefore, the suppression of the penetration is attributable to some B segregating along grain boundaries by equilibrium segregation mechanism. However, effects of solution of B or other elements like oxygen and Fe atoms into Cu-enriched phase should be also examined.

Following experimental results mentioned above, it has been clarified that B tends to enhance grain boundary oxidation, whereas B reduces the amount of Cu-enriched phase at steel/scale interface and the penetration. Therefore, the most beneficial effect of boron on the suppression of the surface hot shortness is observed at the addition of 7ppm.

III-E. Effects of austenite grain size

The surface hot shortness can be reduced by a decrease in austenite grain size.⁸

Fig.2. Effect of boron on microstructure at steel/scale interface (1100°C in LNG combustion gas).

III-F. Effects of atmosphere of heating furnace, heating temperature and deformation rate

The detrimental effect of H₂O in the heating atmosphere has been clarified. The surface hot shortness is suppressed remarkably at 1200 °C comparing to 1100 °C and at very low rate of deformation.⁴

IV. CONCLUSION

Experimental results can be summarized as follows. By physical metallurgy the surface hot shortness due to Cu can be reduced. In order to promote recycling of steels, such physico- metallurgical ways should be applied together with the ways through design of fabrication, separation and smelting.

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