# Suppression of Surface Hot Shortness of Steel due to Cu (+Sn) from Scrap without using Ni

Koji Shibata

Department of Materials Engineering, The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
Fax: 81-35841-8656, e-mail: kshibata@steel.mm.t.u-tokyo.ac.jp
(after 1 April, 2004: 81-42576-4762, kojichiekoshibata@yahoo.co.jp)

Surface hot shortness during hot deformation due to Cu mixed into steels from scrap is the most serious problem in recycling of steel. Tin accelerates this effect of Cu. It is not easy to separate Cu and Sn from steel scrap using physical and chemical methods and to remove these elements from steels by the current smelting process. Therefore, Cu and Sn accumulate in steels with the repetition of recycling. On the other hand, Cu increases strengths and corrosion resistance of steel. Hence the suppression of surface hot shortness due to Cu (+Sn) is important for a decrease in the environmental load by steel. 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. This Cu-enriched phase penetrates into the steel grain boundaries and causes surface cracks. Therefore, there exist tolerable contents of Cu and Sn in commercial steels. In this research, the ways for the suppression of the shortness by controlling microstructures in the vicinity of the steel/scale interface were examined through physical metallurgy.
Key words: steel, recycle, Cu, Sn, microstructure control

## 1. INTRODUCTION

The amount of steel scrap evolved in Japan is expected to be increasing [1]. Therefore, the amount of steel produced using steel scrap will be increased. In addition, the contents of Cu in steel scrap are increasing and the average Cu content in steel scrap is now thought to be around 0.3% [1]. On the other hand, Cu in steels is known to increase steel strength and corrosion resistance. Unfortunately, however, Cu in steels causes surface hot shortness during hot deformation and Sn accelerates this shortness [2]. The mechanism of this shortness has been reported as follows [3-5]. When a steel slab is heated for hot deformation, Cu-enriched liquid phase is formed at the steel/scale interface through selective oxidation of Fe. This Cu-enriched phase penetrates rapidly into austenite grain boundaries during hot deformation, and causes surface cracks. Therefore, there are tolerable contents of these elements, for instance, 0.3% Cu and 0.025% Sn for shape steel [6].

Four ways have been thought to be effective for suppression of the surface hot shortness due to Cu. Namely, (1) to reduce the amount of Cu used in appliances such as automobiles or to promote the easiness of separation of Cu (and Cu alloys) through changing the design of structures and materials, (2) to reduce the amount of Cu in steel scrap as a raw material of steel production through the development of physical and chemical methods of separation, (3) to reduce the amount of Cu in steel through the development of smelting

process and (4) to develop new processing or facilities of steel production which can suppress the oxidation of steel before hot deformation. All of them are important but have not yet been fully reliable.

On the other hand, it is well known that Ni can suppress effectively the surface hot shortness through changing of the amount and shape of the Cu-enriched liquid phase at steel/scale interface [4, 5,7]. But the usage of Ni for a single purpose of the suppression of the surface hot shortness is disliked, because Ni is expensive and a tramp element. Therefore the present author and his co-workers [8-27] are performing the research to develop the fifth way, namely physico-metallurgical way without the usage of Ni (Fig.1). In this paper, their research results will be mentioned.

## 2. EXPERIMENTAL PROCEDURES

Over 50 steels of various contents of P, Si, Mn, S, C, Ni, Sn, B and Cu were melted in vacuum furnaces. Copper contents (mass %) in these steels were mainly 0.5%, but 0.2%Cu steels were also partially melted.
Tensile tests were carried out after heating the specimen at 1373K or 1473K for 1800s in Ar gas. Similar tensile tests were also performed after heating in air, dry air or a gas simulating LNG combustion gas: $74\%N_2$-16% $H_2O$-8% $CO_2$-$2\%O_2$. Strain rate is $2.8 \times 10^{-2}s^{-1}$, when the rate is not mentioned especially.

In order to examine the effects of various elements in steel or in Cu-enriched phase on rapid penetration of the
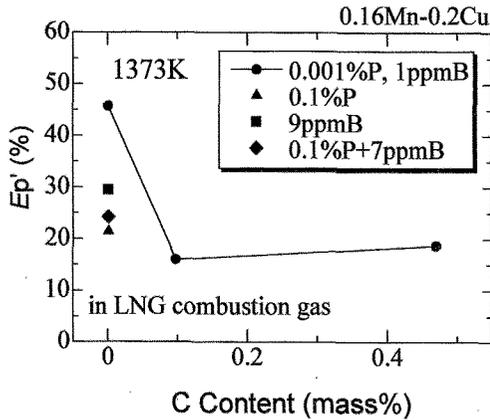
Fig.1 Ways to suppress surface hot shortness and to promote recycling of steel.

Cu-enriched liquid phase into grain boundaries under tensile stress, tensile tests were carried out in Ar gas at 1373K after holding the specimen at this temperature for 30min. In this experiment, round bar specimens implanted with a rod of Cu (tough pitch or oxygen-free) or Cu alloy were used. We will call this experiment as an implant test. Optical microscopy, thermo-gravity measurement, EPMA, AES and ATE (Alpha particle track etching) [28] were also carried out.

## 3. RESULTS AND DISCUSSION
### 3.1 Controlling of microstructures in the vicinity of the steel/scale interface

The present author and his co-workers have examined the effects of heating temperature, heating atmosphere and various elements including impurities in steel on the susceptibility to the surface hot shortness using the parameters which they developed [8]. **Figures 2**[10], 3[25] and 4[20] show some of their results. They [15] summarized such results and proposed three micro-structural controls to suppress the shortness (**Fig.5**). They are controls of (1) morphology (amount, shape and position) of the Cu-enriched liquid phase, (2) easiness of the penetration of the Cu-enriched liquid phase and (3) grain size of austenite.

Silicon exhibits remarkable effect to change the morphology of the Cu-enriched phase [9] and can reduce the Ni content which is necessary to fully suppress the surface hot shortness[10]. Silicon occludes the Cu-enriched phase into scale and reduces the amount of the phase at steel/scale interface. In addition, Si changes the shape of the Cu-enriched phase from planar to globular. Kajitani et al. [29] have reported that liquefied fayalite works to drag the Cu-enriched liquid phase into scale at higher temperatures than 1450K. But the effects of Si on the morphology of the Cu-enriched phase mentioned above can be observed in steels heated at 1373K [9]. Therefore other mechanisms such as internal oxidation of Si [3] or other unknown phenomena are contributable [15].

Phosphorous does not noticeably affect the amount and the shape of the Cu-enriched phase in the case of low [9] and medium [14] carbon steels. In ultra low C steels, however, P changes the

shape from planar to globular [20, 22]. Manganese and S (with Mn) change the morphology of the Cu-enriched phase to restrain the surface hot shortness [25]. Small addition of B also reduces the amount of the Cu-enriched phase and changes the shape of the phase from planar to globular [12, 15, 16]. Carbon reduces the amount of the Cu-enriched phase [19, 21]. Detail reason for the change in the morphology by these elements has remained unknown.

The surface hot shortness tends to occur most severely around 1373K [2, 3, 9]. The amount of Cu-enriched phase is usually smaller in steels hearted at 1473K than at 1373K [2, 9]. This is attributable to the enhancement of diffusion of Cu to the steel matrix and of occlusion [3] at higher temperatures. Hatano et al. [32] examined the effects of pre-heating at higher temperatures and exhibited that such pre-heating increased the amount of the Cu-enriched phase due to the decrease in the solubility of the liquid phase at lower temperatures.

It was reported many years ago that the susceptibility to the surface hot shortness changes with the content of $H_2O$ in heating atmosphere [3,5].

Recently, Maeda et al.[33] reported that microstructure of scale changed noticeably with the content of $H_2O$. Shibata et al.[15] reported a large effect of a small amount of $H_2O$ in air on the susceptibility to the surface hot shortness.



Fig. 2 Effect of Si and Ni on $Ep'$ of 0.1%C-0.5%Mn-0.5%Cu steels [10].



(a)0.002%S          (b)0.02%S

Fig.3 Effect of S on the morphology of Cu enriched phase in 0.1%C-0.5%Mn-0.5%Cu steel [25].

Fig. 4 Effect of C, P and B on $Ep'$ of 0.16%Mn-0.2%Cu steels [20].



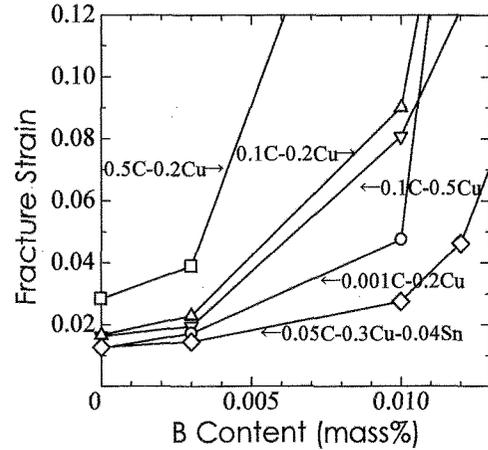Fig.6 Effect of B in Cu on the fracture strain in implant tensile tests of various steels [18].
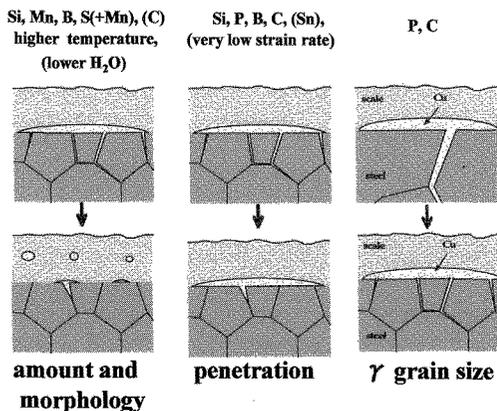


Fig.5 Methods for suppression of the surface hot shortness by physical metallurgy.

Hatano et al. [34] showed that $H_2O$ in the heating atmosphere changed the shape of the Cu-enriched phase to much planar one. Nagasaki et al. [21] also observed similar effect of $H_2O$, although they observed at the same time that the degree of the effect of $H_2O$ was different among steels having different compositions.

### 3.2 Restraining of rapid penetration of Cu-enriched liquid phase

Seo et al. [9] showed that Si and P restrained the penetration of Cu-enriched phase by implant tensile tests using specimens implanted with a rod of pure Cu. Boron [12] and C [14] in steels also suppress the easiness of the penetration of Cu-enriched phase and the effect of B depends on steel composition (Fig.6 [18]).

Stress over some critical value is necessary for Cu-enriched liquid phase to start rapid penetration [9]. McLean [35] proposed the following critical condition that the stress starts liquid embrittlement by rapid penetration of liquid phase:

$$3 \sigma b \geqq 2 \gamma_{SL} - \gamma_b \tag{1}$$

where $\sigma$ is applied stress and $b$ is atomic diameter. If P segregates along the grain boundary and decreases the grain boundary energy, the critical stress is expected to increase. This effect of P is contributable to restraining of the surface hot shortness [34]. Equilibrium grain boundary segregation of B and Si is thought to be negligibly small at 1373K. Therefore, B and Si do not restrain the penetration mainly through their grain boundary segregation. Carbon is thought to be segregate along grain boundaries and this segregation may contribute to the suppression of the shortness, but experimental proof has not been obtained.

The Cu-enriched phase is conceived to contain Si, Fe, P, O and other elements and it was thought that these dissolved elements change the solid-liquid interfacial energy in Eq. (1) to suppress the penetration. Therefore, Shibata et al. [13-24,26,27] melted many Cu-X binary alloys and performed implant tensile tests using specimens implanted a rod of these alloys, although Cu-Si alloy has not been succeed in melting and Cu-C alloy was not melt because the solubility of C in Cu is negligibly small. As a result, they showed that dissolution of Sn [13,27], P [17,26,27] and B [18,20,23,27] in Cu suppress noticeably the penetration of the Cu-enriched liquid phase, although the P content in Cu-enriched phase formed at steel/scale interface by oxidation is too low to reveal this effect [26].

Seo et al. [9] revealed that the susceptibility parameters exhibited the maximum at the strain rate of around $1 \times 10^{-2}s^{-1}$. Implant tensile tests showed the fracture stress increases with an increase in strain rate [13,15,27]. Therefore, the critical stress cannot be explained only by static energy balance such as Eq. (1). Critical stress may be determined also by some dynamical factors like plastic deformation around the crack tip. Sasanuma et al. [13,15] revealed the liquid embrittlement did not occur when dynamic re-crystallization occurs and stress cannot reach to the critical value.

### 3.3 Refining of austenite grain size

Shibata et al. [11] showed the surface hot shortness was restrained with a decrease in grain
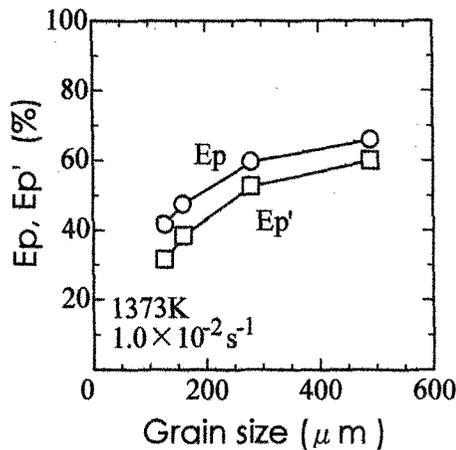
Fig.7 Effect of $\gamma$ grain size on susceptibility to surface hot shortness of 0.1%C-0.5%Mn-0.5%Cu steel [26].

size of austenite when the conditions of oxidation and size of austenite when the conditions of oxidation and stress application are same. Phosphorous [20,26] and C[20,36] decrease the austenite grain size.

## 4. SUMMARY

Physical metallurgy is thought to be feasible as a way for the suppression of the surface hot shortness due to Cu. However, it is not perfect. Therefore, co-usage with other ways is recommended.

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