

Effect of Elements in Copper-enriched Liquid Phase on Surface Hot Shortness in Steels

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Copper contained in steel causes surface hot shortness. When the steel slab containing copper is reheated, copper-enriched phase is formed at the steel/scale interface through selective oxidation and this phase penetrates into austenite grain boundaries of steel during hot working and causes surface cracking. Restraining this effect of Cu is important for recycling of steel. Therefore, the effect of elements in the copper enriched liquid phase on the penetration into the grain boundaries was investigated. The penetration is restrained with increasing content of boron (B) in Cu-B alloy and Cu-Sn-B alloy. Dissolution of Sn into Cu-enriched liquid phase restrains the penetration. Phosphorus in Cu-P alloy is effective in restraining the penetration to some extent. Iron (Fe) and oxygen in Cu-enriched phase have no effect on the penetration.

Key words: recycling of steel, copper-bearing steel, surface hot shortness due to Cu, copper-enriched phase, penetration.

1. INTRODUCTION

Recycling of steels has become an important problem in Japan for reducing CO₂ emission and decreasing the amount of steel scrap. Steel scrap contains tramp elements such as Cu, Sn and Ni[1]. Copper is mixed from the scrap of home electric compliance and cars. Tin is mixed from the scrap of cans. Copper in steel scrap causes surface cracking in hot working. When steel slabs are reheated in oxidation atmosphere for hot rolling, Cu-enriched phase is formed at the steel/scale interface through selective oxidation of Fe. Copper-enriched phase penetrates into austenite (γ) grain boundaries of steel during hot rolling and causes surface cracking by liquid embrittlement. This phenomenon has been called surface hot shortness due to Cu[2]. Tin deteriorates the surface hot shortness. Copper is difficult to be removed in the present steelmaking technique. Therefore, the method for suppression of the surface hot shortness is necessary to be developed.

The authors investigated the effects of additive elements, grain size, atmosphere, temperature and deformation rate on the surface hot shortness[3-6], and proposed three methods for suppression of the hot shortness; (1) reducing the amount of Cu-enriched phase, (2) restraining the penetration of Cu-enriched phase into γ grain boundaries, and (3) refining γ grain size of steel[7].

In this paper, the effect of the elements such as B, P, Sn, Fe and O in Cu-enriched phase on the penetration into grain boundaries was investigated.

2. EXPERIMENTS

The chemical compositions of steels are shown in Table I. The compositions of other elements are around 0.01%Ni-0.001%Ti. The steels were melted in a vacuum furnace and ingots were hot-rolled to 15 mm thick plates.

Table I. Chemical composition of steels (mass%).

	C	Si	Mn	P	S	Cu	Sn
A	0.12	<0.01	0.50	0.019	0.002	0.48	<0.001
B	0.05	0.02	0.28	0.020	0.001	0.31	0.044

In order to evaluate the easiness of the penetration of Cu-enriched phase into γ grain boundaries, hot tensile test was conducted using specimens implanted with a rod of Cu or Cu alloys, as shown in Fig. 1. Hollow specimens were machined from the hot-rolled plates. The length of reduced zone is 20 mm, and the outer and inner diameters are 10 and 4 mm respectively. A commercial rod (13 mm ϕ) of oxygen free copper (OFC) with purity of 99.994% was cold-swaged to a rod of 3.9 mm ϕ . Copper alloys of 100 g were cast in a carbon crucible in Ar gas by using a high frequency induction furnace. The cast alloys were cold-swaged to rods of 3.9 mm ϕ after hot- or cold- forging or rolling.

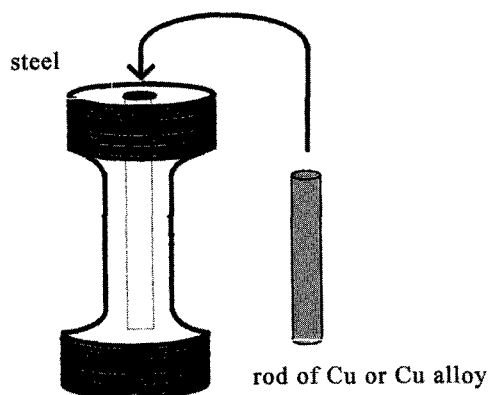


Fig. 1. Schematic illustration of specimen for implant tensile test.

The content of elements in Cu alloys was analyzed by inductivity coupled emission spectrometry (ICPES). Tensile tests were carried out in Ar gas at $1.0 \times 10^{-2} \text{ s}^{-1}$ and $1.67 \times 10^{-4} \text{ s}^{-1}$ after heating at 1373 K for 1.8 ks.

3. RESULTS AND DISCUSSION

3.1 Effects of B and Sn in Cu-enriched phase on penetration

Figure 2 shows the true stress-true strain curves of specimens of Steel A (0.1%C-0.5%Mn-0.5%Cu) implanted with a rod of Cu-B alloy deformed at $1.0 \times 10^{-2} \text{ s}^{-1}$. The dotted line indicates the curve of non-implanted specimen. The stress falls down drastically at a critical strain. The specimen implanted with a rod of OFC was fractured at the strain of 0.03. The fracture strain was increased to 0.04 and 0.05 at the B content of 0.003 and 0.01% respectively. The fracture strain was increased gradually with increasing the B content in Cu-B alloy. The increase in B content of Cu-B alloy restrains the penetration.

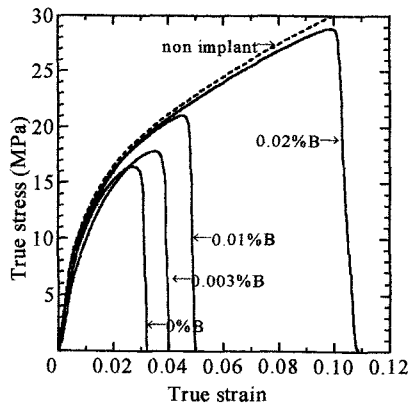


Fig. 2. True stress-true strain curves of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of Cu-B alloy deformed at $1.0 \times 10^{-2} \text{ s}^{-1}$.

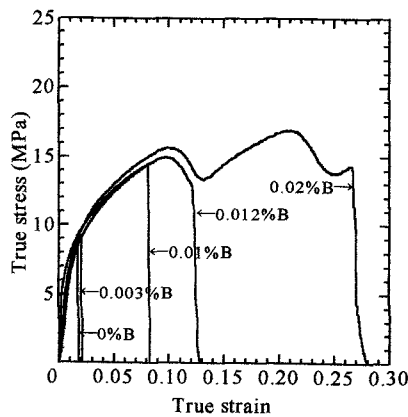


Fig. 3. True stress-true strain curves of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of Cu-B alloy deformed at $1.67 \times 10^{-4} \text{ s}^{-1}$.

Figure 3 shows the true stress-true strain curves of specimens of Steel A implanted with a rod of Cu-B alloy deformed at $1.67 \times 10^{-4} \text{ s}^{-1}$. The fracture strain for the specimen implanted with a rod of Cu-0.003%B is the same as that of OFC. The strain was increased to 0.08 with increasing to 0.01% in B content, and dynamic recrystallization of steel occurs for the B content of 0.012% or higher in Cu-B alloy.

The addition of minor content of B to a 0.1%C-0.5%Mn-0.5%Cu steel suppressed the surface hot shortness[8]. It is thought that the reason is attributed to restraint of the penetration through an increase in B content of Cu-enriched phase.

Figure 4 shows the stress-strain curves of Steel B (0.05%C-0.3%Mn-0.3%Cu-0.04%Sn) implanted with a rod of Cu-B alloy. The fracture strain is 0.03 for Cu-0.01%B. Dynamic recrystallization occurs for the B content of 0.02% or higher in Cu-B alloy. Compared with the steel which does not contain Sn, the effect of B addition is smaller for the steel containing both Cu and Sn.

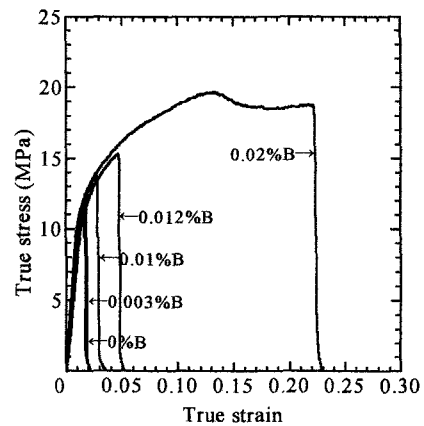


Fig. 4. True stress-true strain curves of specimen of a 0.05%C-0.3%Mn-0.3%Cu-0.04%Sn steel implanted with a rod of Cu-B alloy deformed at $1.67 \times 10^{-4} \text{ s}^{-1}$.

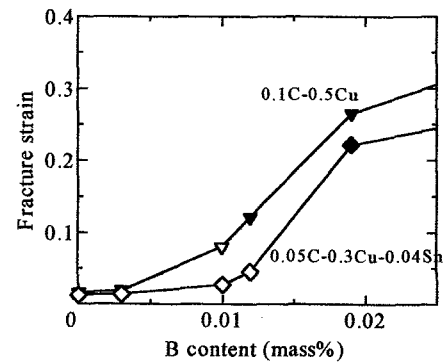


Fig. 5. Effect of B content in Cu-B alloy on fracture strain in implant tensile test of Steels A and B deformed at $1.67 \times 10^{-4} \text{ s}^{-1}$. Solid marks exhibit the occurrence of dynamic recrystallization.

The fracture strain for Steels A and B is compared for the specimen implanted with a rod of Cu-B alloy, as shown in Fig. 5. Dynamic recrystallization occurs in the range plotted by solid marks. The increase in B content of Cu-B alloy for Steel A is more effective than that of Steel B.

Figure 6 shows the stress-strain curves of the specimens of Steel A implanted with a rod of Cu-Sn alloy. The fracture strain was increased slightly with changing a rod of OFC to Cu-5%Sn. The strain was increased with further increase in Sn content of Cu-Sn alloy. It is reported that the ratio of Sn content to Cu in Cu-enriched phase is nearly the same as the ratio of Sn content to Cu in steel[9]. The Sn content is around a tenth of Cu content in recycled steel[1]. Therefore, dissolution of Sn in Cu-enriched phase restrains the penetration.

Figure 7 shows the stress-strain curves of the specimens of Steel B implanted with a rod of Cu-10%Sn-B alloy. The fracture strain was not increased with addition of 0.005%B to Cu-10%Sn alloy, and it was increased to 0.13 for Cu-10%Sn-0.01%B alloy. The increase in B content of Cu-10%Sn-B alloy is more effective in the restraint of the penetration.

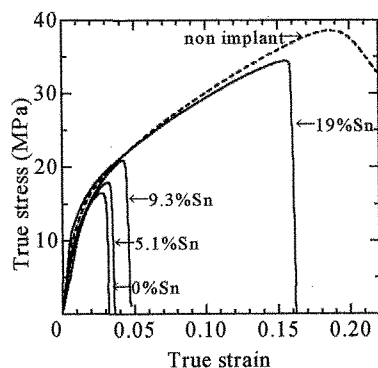


Fig. 6. True stress-true strain curves of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of Cu-Sn alloy deformed at $1.0 \times 10^{-2} \text{ s}^{-1}$.

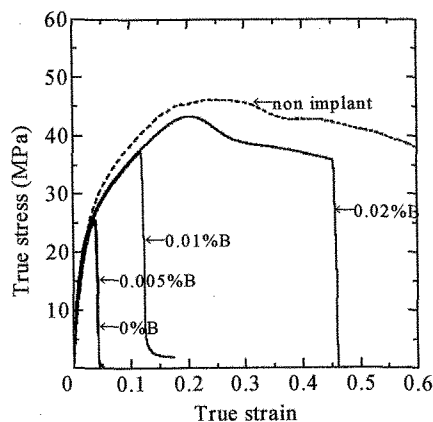


Fig. 7. True stress-true strain curves of specimen of a 0.05%C-0.3%Mn-0.3%Cu-0.04%Sn steel implanted with a rod of Cu-10%Sn-B alloy deformed at $1.0 \times 10^{-2} \text{ s}^{-1}$.

3.2 Effect of P in Cu-enriched phase on penetration

As for the specimens of Steel A implanted with a rod of Cu-P alloy, stress-strain curves are shown in Fig. 8. The fracture strain was not increased with increasing P content up to 0.24%, and it was increased with increasing P content to 0.3% or higher. Kubota et al.[10] reported that the P content in Cu-enriched phase is smaller than 0.15% for a 0.1%C-0.5%Mn-0.5%Cu steel containing 0.1%P. Therefore dissolution of P in Cu-enriched phase has little effect on the restraint of penetration in the surface hot shortness.

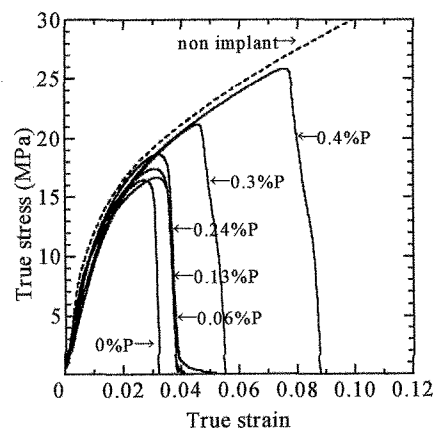


Fig. 8. True stress-true strain curves of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of Cu-P alloy deformed at $1.0 \times 10^{-2} \text{ s}^{-1}$.

3.3 Effects of Fe and O in Cu-enriched phase on penetration

As for the specimens of Steel A implanted with a rod of Cu-Fe alloy, stress-strain curves are shown in Fig. 9. The curve was not varied with increasing Fe content in Cu-Fe alloy to 4.1%. Iron is contained in Cu-enriched phase[9, 11]. The Fe content in the phase is estimated to be about 4% because the solubility of Fe in liquid phase of Cu is 4% at 1373 K[12]. Therefore, the dissolution of

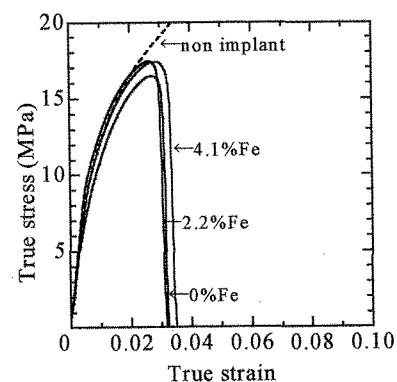


Fig. 9. True stress-true strain curves of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of Cu-Fe alloy deformed at $1.0 \times 10^{-2} \text{ s}^{-1}$.

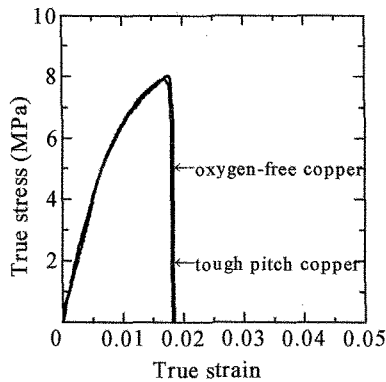


Fig. 10. True stress-true strain curves of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of oxygen free copper and tough pitch copper deformed at $1.67 \times 10^{-4} \text{ s}^{-1}$.

Fe in Cu-enriched phase has no effect on the penetration in the surface hot shortness.

Figure 10 shows the stress-strain curves of specimen of Steel A implanted with a rod of OFC and tough-pitch copper. There is no difference among two curves. Oxygen content of OFC and tough-pitch copper are 5 ppm and <300ppm respectively. Oxygen has no effect on the penetration in the range of O content up to 300 ppm.

3.4 Penetration of liquid phase into grain boundaries

For the specimen of Steel A implanted with a rod of OFC deformed at $8.3 \times 10^{-4} \text{ s}^{-1}$, fractured surface is shown in Fig. 11. All of the surfaces were intergranular from inner side of specimen (upper part of figure) to outer side (lower part of figure). Penetration of liquid Cu proceeds along γ grain boundaries.

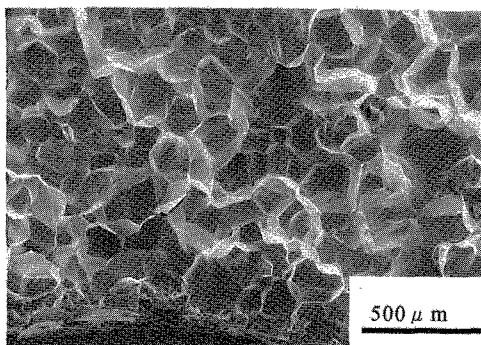


Fig. 11. Fractured surface of specimen of a 0.1%C-0.5%Mn-0.5%Cu steel implanted with a rod of OFC deformed at $8.3 \times 10^{-4} \text{ s}^{-1}$.

McLean[13] proposed the criterion that penetration of liquid metal into a grain boundary occurs under tensile stress. The stress σ required for penetration is given by following equation.

$$3 \sigma b \geq 2 \gamma_{SL} - \gamma_b \quad (1)$$

where γ_{SL} is solid/liquid interface energy, γ_b is grain boundary energy and b is atomic diameter. When some elements segregate along grain boundaries, the stress is expected to increase through a decrease in γ_b . When additive elements are dissolved in Cu-enriched phase and increase γ_{SL} , the stress is increased. Elements in steel can be dissolved in Cu-enriched phase if they have solubility in Cu liquid phase. Boron and Sn are thought to be effective in the restraint of penetration of Cu-enriched phase into grain boundaries through increasing γ_{SL} .

4. CONCLUSION

The easiness of penetration of Cu and Cu alloy liquid phase into austenite grain boundaries of low carbon steels was investigated.

- (1) The increasing B or Sn content in Cu alloys restrains the penetration through increasing solid/liquid interface energy. Boron is effective by a small amount of addition.
- (2) The increase in B content in Cu-10%Sn-B is more effective in the restraint of the penetration.
- (3) Phosphorus is effective in the restraint of penetration when the P content in Cu alloy exceeds the critical value of 0.3%. But the P content dissolved in Cu-enriched phase is smaller than the critical value.
- (4) The content of Fe and O in Cu-enriched phase has no effect on the penetration.

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