

## Copper Elimination from the Molten Steel by Addition of Hydronitrogens\*

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**Abstract:** A novel method has been proposed to remove copper from molten steel by adding the compounds of hydrogen and nitrogen into the melt at normal pressure. Feasibility experiments were carried out in Mo-wire resistance furnace at 1 600 °C. The copper content of about 400 g 45 steel were reduced from 0.60% and 0.57% to 0.41% and 0.51% with 3.25 g and 1.20 g NH<sub>4</sub>Cl respectively, while the copper contents of about 300 g steel melt were reduced from 1.15% and 0.61% to 0.90% and 0.56% with 4.10 g and 2.00 g NH<sub>2</sub>CONH<sub>2</sub>. These results indicate that the proposed method is very promising to be put into practical and worthwhile of further study.

**Key words:** molten steel, copper removal, hydronitrogens

Steel scrap is one of preferable charge materials for steelmaking owing to its thermodynamic state relatively close to that of the final valuable materials. Recycling of steel scrap leads to the omission of steelmaking technological steps such as coke making, reduction of ore, and sintering, and results in an energy saving of one-third to two-thirds with respect to the amount required to make steel from iron ore, and can eliminate the environmental pollution associated with the above steps and the disposal of huge amount of ferrous scrap. However, a large proportion of available steel scrap is increasingly becoming inferior for steelmaking because of high residuals of copper, tin, and zinc contaminants in the consumer scrap. Copper and tin have a detrimental effect in steel during fabrication and application, while zinc contributes to furnace operational and dust proposal problems<sup>[1,2]</sup>. Furthermore, copper can not be eliminated during normal melting and refining processes, and tends to build up in steel in scrap recycling. A point may be reached in the near future when thousands of millions tones of obsolete steel scrap can not be recycled without a treatment process to remove these residual elements.

Due to the growing concern about the residual elements in scrap recycling, several investigations have been reported for the removal of copper from ferrous scrap<sup>[3~10]</sup>. Of these, the decuprization method reported in literature [10] shows originality. The

copper content in molten steel was reduced from about  $2.5 \times 10^{-3}$  to  $(0 \sim 10) \times 10^{-6}$  in 90 min by NH<sub>3</sub> blowing under reduced pressure lower than 2.67 kPa. However, the experiments in question were carried out in a vacuum induction furnace. Therefore, it is not very convenient to treat a large amount of steel scrap by virtue of the above method in practical steel production. In this investigation, an alternative approach was proposed to remove copper in steel melt by adding compounds of hydrogen and nitrogen, and the feasibility experiments were conducted at normal pressure in argon atmosphere.

### 1 Experimental

The experiment was conducted in a Mo-wire resistance furnace under a protective atmosphere of Ar at normal pressure, shown schematically in Fig. 1. 300 ~ 400 g of 45 steel was melted in an alumina crucible of 36 mm inner diameter and 60 mm height. The temperature of steel melt was kept at 1 600 °C by an JWT temperature controller.

At the beginning of each experiment, a given amount of pure copper was added into the molten steel. After homogeneous dissolution of copper, the first sample of steel was taken by a thin quartz tube for analysis of its initial copper content.

Then a feeding rod of about 7 mm outside diameter,

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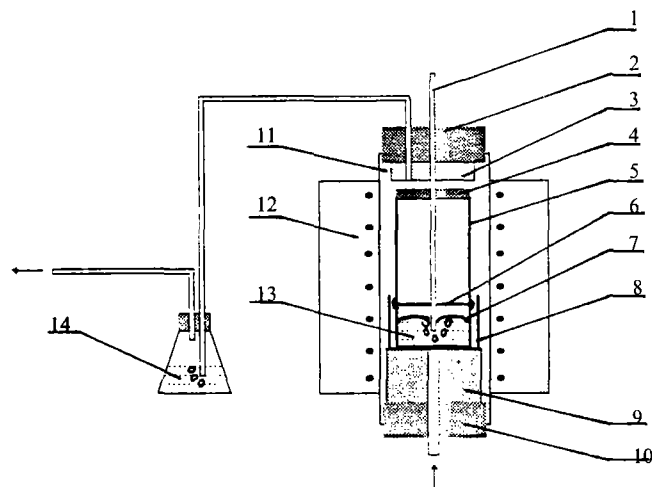


Fig.1 Experimental arrangement for decopperization

- 1 Feeding hallow rod; 2 Stopper;  
 3 Insulating brisk; 4 Graphite cover;  
 5 Al<sub>2</sub>O<sub>3</sub> tube; 6 Cement;  
 7 Al<sub>2</sub>O<sub>3</sub> crucible; 8 Graphite crucible;  
 9 Support; 10 Stopper;  
 11 Al<sub>2</sub>O<sub>3</sub> tube;  
 12 Mo-wire resistance furnace;  
 13 Steel melt; 14 Gas scrubber

containing a given amount of NH<sub>4</sub>Cl or NH<sub>2</sub>CONH<sub>2</sub> powders as decopperizing agent in a drilled cavity at the lower end of the rod as shown in Fig. 2, was inserted into the molten steel to about 30 mm in melt depth. Being kept for a few seconds until the complete consumption of the agent, the rod was taken out immediately. Then the second feeding rod was inserted into the melt with the same way as last insertion, and so was done the others. Samples were taken at regular intervals of insertions, 3~4 g of molten steel was taken each time, to analyze the copper content of the steel melt by means of atomic absorption spectrum. The off-gas entered into a gas scrubber and was absorbed by the deionized water, which was spectroscopically analyzed for the copper and iron concentrations. The inserted ends of feeding rods were cut off to determine the copper contents on the surfaces of the rods with EDS.

The conditions of each experiment are represented in table 1.

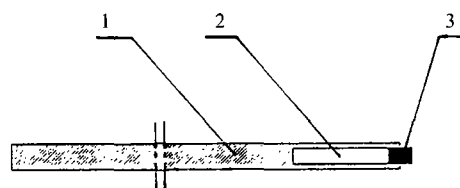


Fig.2 Feeding hallow rod

- 1 Steel rod; 2 Decopperizing agent; 3 Steel spigot

with different violence depending on the quantity of the added reagent and the experimental temperature. Almost at the same time, a lot of gas bubbles appeared in the absorbing water and white smog could be seen above the surface of the water in the gas scrubber. Having taken out the feeding rod and quenched it in cooling water, we found that there were many lines and flecks of copper on the surface of the feeding rod. This can be seen in the photograph of the cut end of inserted rod in Fig. 3. After absorption of the off-gas, the pH value of the absorbing water turned out to be 2~4 for the experiments with NH<sub>4</sub>Cl, while the pH

Table 1 The experimental conditions

Experiment number	Mass of steel melt/g	Decopperizing agent	Mass of decopperizing agent/g	Mass of Decopperizing agent each time/g	Agent-adding times each sample
1	424	NH <sub>4</sub> Cl	3.25	0.13	5
2	394	NH <sub>4</sub> Cl	1.20	0.02	10
3	282	NH <sub>2</sub> CONH <sub>2</sub>	4.10	0.40	1
4	283	NH <sub>2</sub> CONH <sub>2</sub>	2.00	0.10	5

## 2 Results and Discussions

On insertion of a feeding rod, the steel spigot of about 0.5g at its end closing the cavity of the rod (see Fig. 2), was melted, and the gas of decopperizing agent jetted into the melt in no time, causing a splash of the melt

value was 9 in the case of NH<sub>2</sub>CONH<sub>2</sub>. The experimental results obtained for removal of copper from the melt by NH<sub>4</sub>Cl and NH<sub>2</sub>CONH<sub>2</sub> are represented in table 2. For comparison of the effects of these two decopperizing agents, the decreases of copper contents of the melts with the addition of NH<sub>4</sub>Cl and

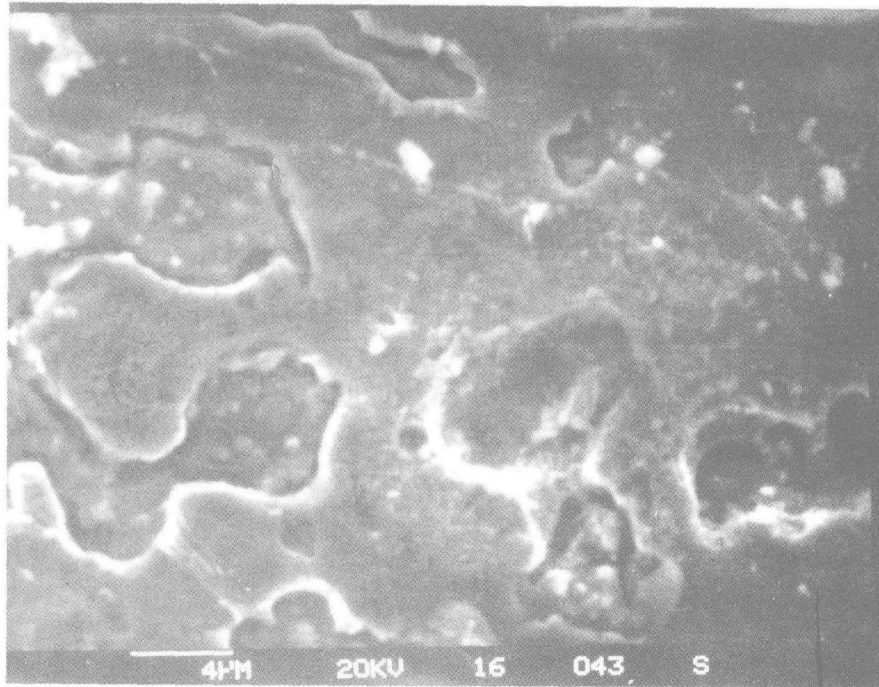
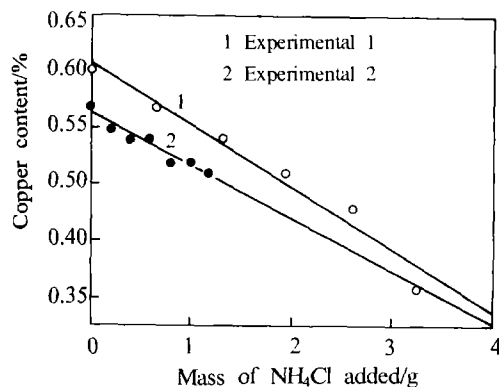
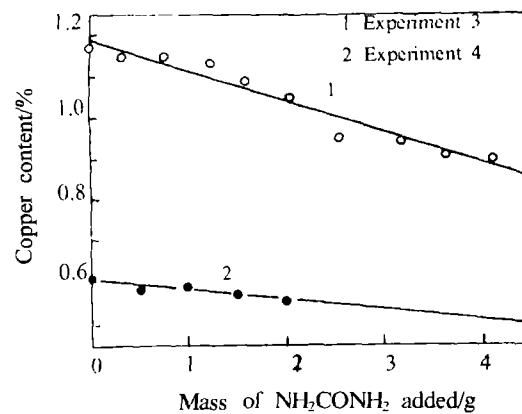


Fig.3 SEM photograph on the surface of the section of feeding rod

Table 2 Experimental results

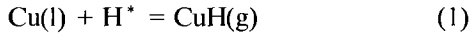
Experiment number	Copper content/%		Decopperizing efficiency/%	Mass of copper removed one g of decopperizing agent/g
	Initial	Final		
1	0.60	0.41	31.7	0.25
2	0.57	0.51	10.5	0.20
3	1.15	0.90	21.7	0.17
4	0.61	0.56	8.2	0.17

Fig.4 Copper content of steel melt as the function of the mass of NH<sub>4</sub>Cl addedFig.5 Copper content of steel melt as the function of the mass of NH<sub>2</sub>CONH<sub>2</sub> added

NH<sub>2</sub>CONH<sub>2</sub> are shown graphically in Fig. 4 and Fig. 5 respectively. Both NH<sub>4</sub>Cl and NH<sub>2</sub>CONH<sub>2</sub> are good for copper removal of steel melt. However, the decopperizing efficiency of NH<sub>4</sub>Cl is better than that of NH<sub>2</sub>CONH<sub>2</sub>. One gram of NH<sub>4</sub>Cl could remove 0.20 ~ 0.25 g of copper from the melt, while one gram of NH<sub>2</sub>CONH<sub>2</sub> could only remove 0.17 g. Furthermore, the line for NH<sub>4</sub>Cl still presents considerably large slope

at the final of the experiments. This implies that the copper content can be reduced further to a relatively low level as long as NH<sub>4</sub>Cl is added constantly. The copper removal of NH<sub>4</sub>Cl is attributed to the following two constituent gases. On addition of NH<sub>4</sub>Cl into the steel melt at high temperature, it will decomposed immediately into HCl and NH<sub>3</sub> gases. NH<sub>3</sub> will in turn crack into H<sub>2</sub> and N<sub>2</sub> in no time. It is possible that H<sup>+</sup>

and  $N^*$  in the nascent state exist within the relaxation period between the decomposition of  $NH_3$  and the formation of  $H_2$  and  $N_2^{[10]}$ . Because of the high thermodynamic potential of  $H^*$ , it could react with copper on an active site of the melt surface and a volatile compound will form as follows

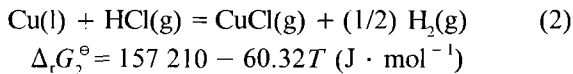


and liberate directly from surface of the melt to gaseous phase. A passing gaseous nitride can not be completely denied. The formation of these volatile compounds will promote the vaporization of copper in the steel melt.

Because of its instability, which is indicated by the positive value of the standard Gibbs free energy of formation of the compound  $CuH^{[10]}$ , it will decompose into gaseous  $H_2$  and solid copper depositing on the wall of the reactor and the surface of the feeding rod (see Fig. 3). The EDS data of the cut rod indicates that the content of the copper depositing on the surface of the rod is as high as 20% to 30%.

The second contribution of ammonia decomposition to the vaporization of copper is the increase of the gas-metal interfacial area by the formation of enormous amount of very fine bubbles and by the stirring of the melt during the motion of the bubbles.

At the same time, HCl gas will chlorinate the copper in the melt through the following reaction



The equilibrium constant of reaction (2) at 1 600°C is

$$K_2 = \rho_{CuCl} \cdot \rho_{H_2}^{1/2} / \rho_{HCl} = 0.058.$$

This shows that a certain amount of copper in the melt can be evaporated as the volatile form of  $CuS$ .

$NH_2CONH_2$  will decompose into  $CO$ ,  $H_2$ , and  $N_2$  after being added into the melt. The mechanism to evaporate copper is similar to that of  $NH_3$ .

$NH_4Cl$  possesses double effects of copper removal, therefore it is superior to  $NH_2CONH_2$  in this aspect. However, there is more or less of iron loss due to the chlorination of base iron when  $NH_4Cl$  is added into

the steel melt, for the spectroscopic analysis of the water in the exhaust gas scrubber shows that there is  $2.3 \times 10^{-5}$  of Fe in it besides  $7.0 \times 10^{-7}$  of Cu, while there was hardly any Fe in the absorbing water when urea was used.

### 3 Conclusion

The approach proposed in this investigation to remove copper by adding hydronitrogens into steel melt is feasible. However, further investigation are needed to improve the decopperizing effect of these agents and to understand thoroughly their decopperizing mechanism

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