Transactions of the Materials Research Society of Japan 24 [3] 337-340 (1999)

Removal of Copper and Other Impurities from Scrap Iron

Ryokichi Shimpo and Osamu Ogawa*
Musashi Inst. of Tech. Setagaya-ku, Tokyo, 158-8557, Japan
Fax: +81-3-5707-2105,
*Univ. of Tokyo, Bunkyo-ku, Tokyo, 113-8656, Japan
e-mail: shimpo@se.me.musashi-tech.ac.jp, oogawa@ibm.net

Recycling of scrap iron will save the consumption of material resources and energy, and will reduce CO_2 generation. However, impurities mixed into the scrap iron such as copper or tin may act harmful for the properties of recycled steel. The authors have been proposing several methods for removing copper in scrap iron. For the copper removal from molten iron, a method using a sulfide flux of the Al_2S_3-FeS system is presented. The flux has a higher ability for extracting copper than the other fluxes such as the Na_2S-FeS system. Another advantage of this method is the iterative use of the flux by recovering copper from it. A method using lead bath is also presented for the removal of copper and other impurities from solid scrap iron. The extracted copper in the lead bath can be transferred to Al-Cu alloy quite easily, and then the lead bath is capable to be iterated. This method is considered economical because the energy consumption and required amounts of lead and aluminum are small, overall system is simple, and other impurities such as tin, antimony, and precious metals are simultaneously recovered.

Key words: recycling, scrap iron, copper, tramp element

1. INTRODUCTION

Removals of impurities are the important problems on recycling. In most of metal scraps, iron is the dominant element, and it is generally considered that the recycling of scrap iron is comparatively easy. Nevertheless, once impurities such as copper, tin, and antimony, which are called as tramp elements, are dissolved into molten iron, it is quite difficult to remove them economically, and they act harmfully against the characteristics of recycled steel; for example, causing hot shortness in hot rolling operation. Therefore, scrap iron is generally recycled to low grade steels, and little scrap iron is used for the production of high grade steels. Nowadays, the amount of scrap iron which is not recycled is increasing, so, if effective techniques for removing the impurities form scrap iron are established, the amount of recycled iron will increase by using them for the production of higher grade steels. The development of the recycling of scrap iron will give us the benefits of saving the energy consumption and decreasing CO_2 generation by reducing the ratio of iron product by blast furnace. Moreover, the development of the techniques for removing impurities will enable the recycle use of the scraps such as electric goods which contain more ratios of impurities, and it will reduce the amount of wastes and enable the recovery of valuable elements from the scraps. The recovery of precious metals such as gold or platinum will be an important item for the economical point of view.

Accordingly, the techniques for removing impurities from scrap iron, especially copper removal, are important. To date, numbers of ideas for copper removal from scrap iron have been proposed[1]. Techniques of vacuum distillation, vaporization as copper chloride, and sulfide slagging by Na_2S-FeS flux[1,2] have been presented for copper removal from molten iron, and preferential melting, extraction by metal bath such as aluminum[3], and dissolution into ammonia solution are listed for that from solid scrap iron. However, no economical process has been established because of low efficiency of copper removal, requirement for high cost, or high energy consumption.

In this paper, two techniques are introduced which are more effective and economical; one is a sulfide slagging using Al_2S_3-FeS flux for copper removal from molten iron, and the other is a method using both lead and aluminum from solid scrap iron.

2. COPPER REMOVAL FROM MOLTEN IRON USING Al_2S_3-FeS FLUX

Copper removal from molten iron is a especially difficult technique because copper is usually nobler element than iron and because the copper removal should be conducted on keeping the molten iron as metallic state; if iron is altered to ionic or compound forms in the course of recycling, much amount of energy will be required for reducing them again. Only as to the formation of sulfides, copper behaves baser than iron. Accordingly, copper removal methods using sulfide fluxes such as the Na_2S-FeS system have been investigated so far[1,2]. Among them, the authors have discovered that a new sulfide flux of the Al_2S_3-FeS system has a higher ability for extracting copper from molten iron[4,5].

The reaction for copper extraction from molten iron with sulfide fluxes is expressed as follows:

$$FeS_{(flux)} + 2Cu_{(molten\ iron)} \rightarrow Cu_2S_{(flux)} + Fe_{(molten\ iron)}$$

The Al_2S_3 in the flux plays a role of promoting the reaction; that is, it decreases the activity coefficient of Cu_2S in the flux and increases that of FeS. Fig.1 shows the relationship between the flux composition and the equilibrium copper distribution ratio,

L_{Cu}= (mass%Cu in flux) / [mass%Cu in molten iron],

between the Al_2S_3-FeS flux and carbon-saturated molten iron. The maximum value of the L_{Cu} for the Al_2S_3-FeS flux is around 28 which is higher than that of the Na_2S-FeS flux of around 24. Figs.2 and 3 show the sulfur and aluminum contents in the carbon-saturated molten iron equilibrated with the Al_2S_3-FeS flux, respectively.

Another advantage of this Al_2S_3-FeS flux is that the copper extracted into the flux can be recovered easily in comparison with other sulfide fluxes, and the flux can be iteratively reused for copper extraction. At first, after separating from molten iron, FeS in the flux is reduced by the addition of metallic aluminum according to the

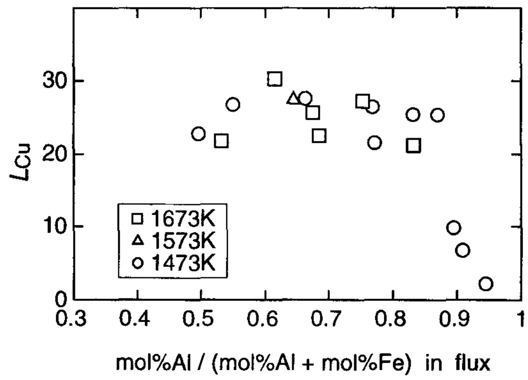

Fig.1 Relation between the composition of the Al_2S_3-FeS flux and the copper distribution ratio, L_{Cu}

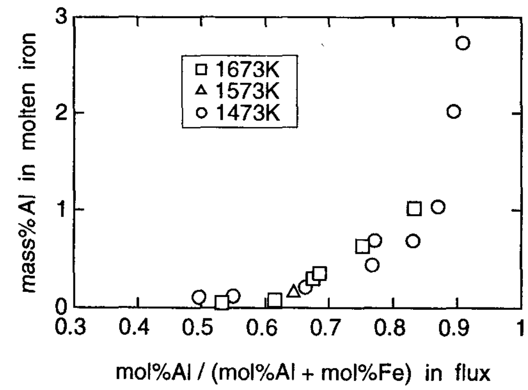

Fig.2 Relationship between the flux composition and aluminum content in the molten iron phase

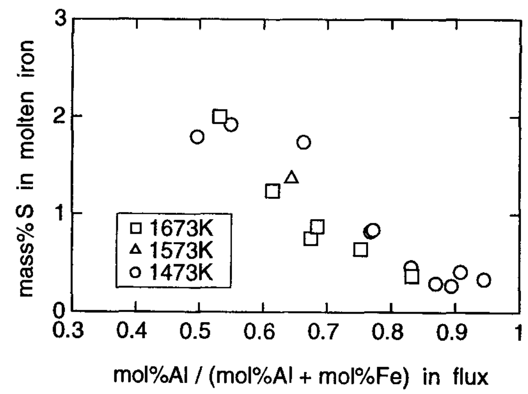

Fig.3 Relationship between the flux composition and sulfur content in the molten iron phase

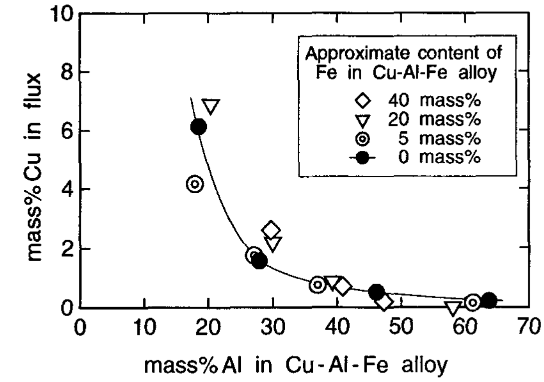

Fig.4 Relationship between aluminum content in the Cu-Al-Fe alloy and copper content in the Al_2S_3-FeS-Cu_2S flux at 1473K

following reaction:

$$3FeS_{(flux)} + 2Al \rightarrow Al_2S_{3(flux)} + 3Fe$$

After separating the generated iron from the flux, Cu_2S in the flux is also reduced by additional metallic aluminum:

$$3Cu_2S_{(flux)} + 2Al \rightarrow Al_2S_{3(flux)} + 6Cu$$

In the actual reaction, copper is recovered in the form of Cu-Al-Fe alloy (Fig.4). The flux after the copper recovery can be iterated to the copper extraction from molten iron where sulfur sources such as FeS_2 is added to supplement FeS in the flux.

An example of the flow diagram of copper removal process from molten iron with the Al_2S_3-FeS flux is shown in Fig.5. Three stages of copper extraction are employed. It is estimated that about 10 to 20 kg of metallic aluminum will be required for reducing the

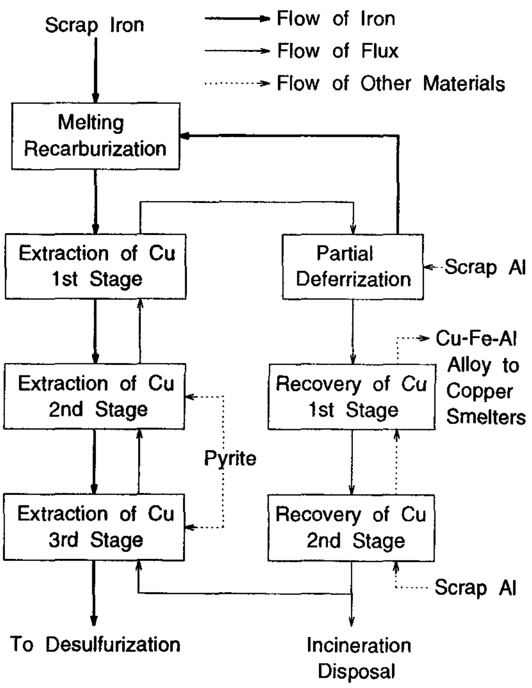

Fig.5 A schematic flow diagram of copper removal from molten iron using the Al_2S_3 - FeS flux

copper content from 1 mass%Cu to less than 0.1 mass% Cu per 1 ton of molten iron. The required amount of FeS_2 is estimated to be from 20 to 40 kg per 1 ton of molten iron. It is desirable that the molten iron is saturated with carbon because it increases the activity coefficient of copper and lowers the sulfur dissolution in the molten iron.

As to other impurities than copper, possibilities of the removals of Sn, Sb, and Ni were experimentally examined using the Al_2S_3-FeS flux. However, the individual distribution ratios obtained were very low values, L_{Sn}=0.3, L_{Sb}= 0.1, and L_{Ni}=0.07, respectively. The removals of these impurities are, therefore, considered to be difficult by the slagging method though removal by the vaporization in the sulfide forms such as SnS, SbS, or Sb_2S_3 is suggested. The other disadvantages of this method are that a desulfurization operation will be required after the copper removal and that the oxidation of the flux must be avoided using an inert gas flow because Al_2S_3 is easily oxidized.

3. IMPURITY REMOVAL FROM SOLID SCRAP IRON USING LEAD AND ALUMINUM

Comparing with the difficulty of copper removal from molten iron, that from solid scrap iron seems easier. Pb bath has long been a candidate for a solvent for copper extraction from molten iron because molten iron and molten lead are almost immiscible with each other. However, this method was evaluated to be non-economical because the copper distribution ratio between molten lead and iron is as low as around 1 to 2, and methods for separating copper from the lead phase have not been discussed so far. So, it has been said that more than 1000 kg of virgin lead metal will be required for the copper removal treatment of 1 ton of scrap iron.

Against this evaluation, the authors have presented an improved method[5] in which copper extraction by lead bath is conducted from solid scrap iron instead of molten iron and lead bath is iteratively used by removing the extracted copper in the lead bath to Al-Cu alloy. This technique is attributed to the characteristics that aluminum has higher affinity for copper than for lead, and that aluminum and lead have a miscibility gap. Fig.6 shows the solubility of copper in molten lead in equilibrium with molten Al-Cu alloy. From this figure, it is confirmed that the copper content in the molten lead can be reduced to less than 0.1 mass% even if the copper content in the Al-Cu alloy after the copper recovery from the lead bath becomes as high as 50 mass%. It is also confirmed from Figs.7 and 8 that the aluminum content in the molten lead and the lead content in the Al-Cu alloy both decrease according to the increase of copper content in the Al-Cu alloy up to 70 mass%Cu.

Fig.9 is a schematic process flow diagram of copper removal from solid scrap iron using both lead bath and Al-Cu alloy. By iterating the molten lead between scrap iron and the Al-Cu alloy, the copper removal can be conducted efficiently even at a single stage of extraction. Assuming that the obtained Al-Cu alloy contains 50 mass%Cu and 1 mass%Pb, the amount of lead transferred to the alloy is calculated to be 0.2 kg per 1 ton of scrap iron initially containing 1 mass%Cu. Though other lead losses in the forms of dust and dross

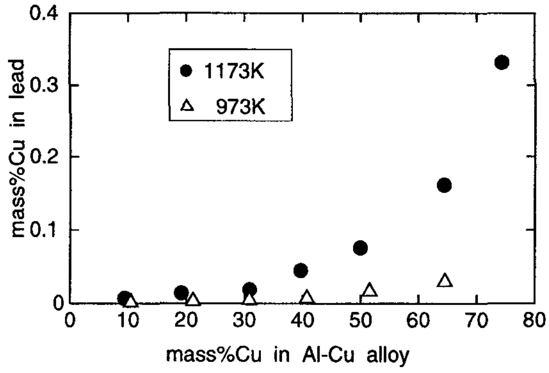

Fig.6 Relation between the copper content in molten lead and that in Al-Cu alloy in equilibrium

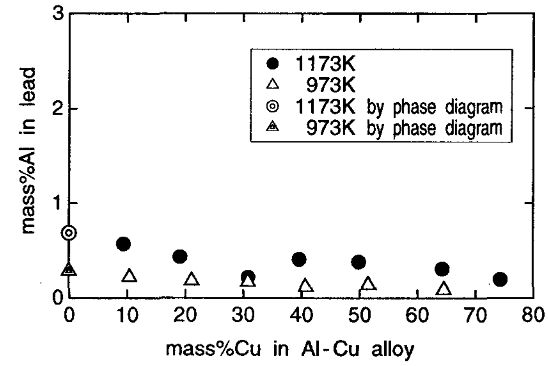

Fig.7 Experimental result on the relation between the aluminum content in molten lead and copper content in Al-Cu alloy

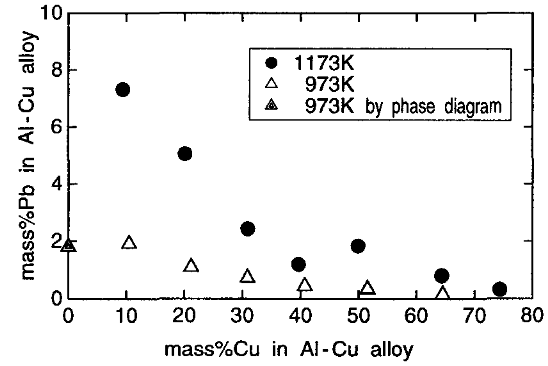

Fig.8 Experimental result on the relation between the lead content and copper content in Al-Cu alloy

are also considered, they can be recovered by sending them to lead or copper smelters. The required amount of aluminum is 10kg / ton scrap in the above condition. In case the scrap iron contains aluminum, the required amount of aluminum can be reduced, and when the solid scrap contains more aluminum than copper, additional metallic aluminum will be unnecessary. A similar copper removal process may be proposed in which copper is directly extracted from scrap iron into aluminum[3]. However, the process will require much more amount of aluminum or more number of copper extraction stages.

In the case of other impurities than copper, many kinds of metallic elements of comparatively low melting points can be extracted from solid scrap iron to the lead bath, and some of them can be transferred to the Al-Cu alloy efficiently. Table I shows results of evaluations for distribution ratios of impurities between molten aluminum and lead calculated by thermodynamic data[6], where the distribution ratio for an impurity element M is defined as follows:

L_M= (mass%M in molten Al) / (mass%M in molten Pb)

Precious metals of Au and Ag are expected to be recovered efficiently into Al-Cu alloy together with Cu. Though Sn and In are evaluated to be hardly transferred to the Al-Cu alloy, they can be removed from lead bath in oxide forms by partial oxidation; many kinds of elements, which are easier to be oxidized than Pb, such as Sb, Ni, and Zn can also be removed from the lead bath. Elements of Hg, As, Zn, and Cd are likely to be removed by evaporation. Though Bi is considered to be hardly removed from lead bath, Bi has a characteristics similar to Pb, and is hardly dissolved into molten iron. Though metallic elements of high melting points such as Cr or Ti are difficult to be extracted to lead bath, they can be removed by oxidation after scrap iron is melted. The most difficult elements to be removed may be Co because its solubility in the lead bath is very low just as Fe and is more hardly to be oxidized than Fe.

When scrap iron after the lead bath treatment is melted, most of lead stuck on the surface of the scrap will separated. If a little amount of Pb solubility in the molten iron becomes a problem, vacuum distillation or vaporization by lead chloride adding chlorine source such as $FeCl_2$ or Cl_2 will be effective.

The Al-Cu alloy is sent to copper smelters together with recovered valuable elements and they are recycled there. Another idea is a recovery of reducing energy included in metallic aluminum before sending to smelters by composing an electric cell in which the solidified Al-Cu alloy is employed as anode.

As mentioned above, this copper removal method seems more efficient because the system is comparatively simple, required resources and energy consumption are small, and various impurities are simultaneously removed. The efficient recovery of precious metals will be an important point for making the process economical. Though lead is a poisonous metal, environment pollution will be avoided by making the lead flow in the process more closed one.

4. SUMMARY

Two copper removal methods are presented. One is a sulfide slagging process for copper removal from molten iron with the Al_2S_3-FeS flux, and procedure of the iterative use of the flux is exhibited. The process seems somewhat complicated and may not be employed for the time. However, any of copper removal methods from molten iron will be essential in future because copper content in recycled copper can not avoid increasing.

The other method is for impurity removal from scrap iron using Pb and Al which seems simpler and easier than the removal from molten iron. Other impurities including precious metals can be recovered together with copper and it will make the process more economical.

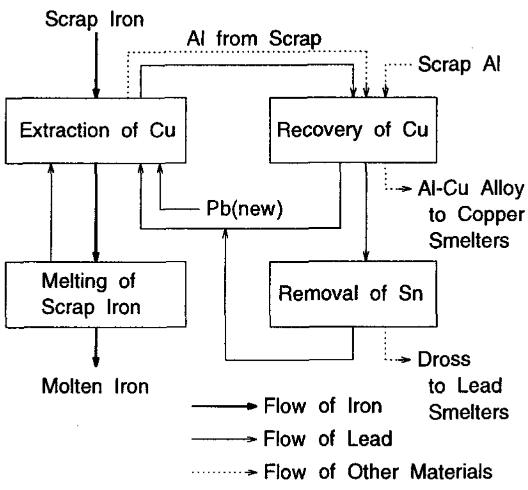

Fig.9 A schematic flow diagram of copper removal from solid scrap iron using Pb and Al

Table I Calculated values of distribution ratio L_M between aluminum and lead at 1273K from thermodynamic data[6]

Element	Solubility in Pb	Activity coefficient		Estimated
		γ^0 in Pb	γ^0 in Al	L_M
Au	95 mass%	0.31	8.1×10^{-5}	30000
Cu	80 mass%	6.9	0.037	1400
Ag	100%	2.0	0.34	65
Ga	100%	6.8	1.1	49
Sn	100%	6.0	3.3	14
In	100%	0.96	8.0	0.92
Bi	100%	0.63	18	0.27

REFERENCES

1. I. Jimbo, M.S. Sulsky, and R.J. Freuehan, *Proc. W.O. Philbrook Memorial Symp.*, ISS-AIME, Warrendale, PA, (1988), pp. 133-144
2. C. Wang, T. Nagasaka, M. Hino, and S. Ban-ya, *Iron Steel Inst. Jpn. Int.*, vol.31, (1991), pp.1309-15
3. M.Iwase and K.Tokinori, *Steel Research*, vol.62, (1991), pp.235-239
4. R. Shimpo, Y. Fukaya, T. Ishikawa, and O. Ogawa, *Metallurgical and Materials Transactions B*, vol 28B, (1997), pp. 1029-37
5. R. Shimpo, T. Ishikawa, O. Takenouchi, and O. Ogawa, *Third International Conference on ECOMATERIALS*, (1997), A4-5, pp.177-180
6. O. Kubaschewski and C.B.Alcock, *Metallurgical Thermochemistry*, 5th ed., Pergamon Press, Oxford, (1979)

(Received December 11, 1998; accepted March 18, 1999)