Mem. Fac. Sci. Eng. Shimane Univ.
Series A
30, pp. 99-114 (1997)

Research Activities on Removal of Residual Elements from Steel Scrap in Japan

Hiroyuki KATAYAMA (*Interdisciplinary Faculty of Science & Technology*)
Nobuo SANO (*The University of Tokyo*)
Minoru SASABE (*Chiba Institute of Technology*)
Shigeki MATSUOKA (*Daido Special Steel Co.*)

(Received December 31, 1996)

Synopsis:

The generation of obsolete scrap in Japan is increasing and expected to account for more than 40% of total steel production by the year 2010. To make effective use of all of this steel scrap generated, the deterioration of hot workability of steel products may arise as a problem caused by copper and tin accumulations. This paper selects and summarizes the results of research on the removal of residual copper and tin from steel scrap from among the research activities of two groups formed concerning the utilization of steel scrap - Committee for Removing Residual Elements from Steel Scrap of the Iron and Steel Institute of Japan (ISIJ) and Scrap Recycling Technology Research Project of the Japan Research and Development Center for Metals (JRCM).

(1) If Japan is to use all of the steel scrap generated as feed material for steel production in 2010, the average removal ratio will have to be improved to about 55% for copper and 30% for tin.

(2) When copper is present mixed with steel, mechanical separation following shredding (including cryogenic processing) is the most practical method for removing copper from steel scrap. Separation of liquid copper from solid steel by adjusting the atmosphere conditions in the steel scrap preheating step, selective melting of copper in an aluminum bath, and selective dissolution of copper by a wet process with ammonia, for example, also have potential for practical application. Removal of copper by vaporization under vacuum promoted by the vigorous CO bubble formation was studied as the method for separating copper dissolved in steel. A combination of these methods is expected to achieve the target copper removal ratio of 55%.

(3) Unlike copper, tin is low in content and less advantageous to be recovered. The addition of another step for the sole purpose of removing tin from steel scrap is not economically justified. The method of separating the tin coating as oxide film in the steel scrap preheating step and the method of vaporizing tin as stannous sulfide (SnS) in the steel scrap melting step were investigated. Each method was confirmed to be capable of removing tin from steel scrap by about 40%.

(4) A total process was proposed that is composed of steel scrap preheating, melting and dust treatment and removing these residual elements from steel scrap. The total process is planned for evaluating each technology as a combined system.

1. Introduction

Of the impurities contained in steel scrap, copper, tin, antimony and arsenic are the elements difficult to be removed in conventional steelmaking processes. Zinc and lead are relatively easy to be removed from steel scrap by vaporization but involve various problems to be studied when dust disposal is taken into account. These elements are generically called residual elements.

How to remove the residual elements from steel scrap and change them into such form that they are stable and exert no adverse effect on the environment will be an important research issue for future steelmaking processes. This issue has not been systematically studied in the past.

In Japan, two groups initiated cooperative research activities on this subject.

The Committee for Removing Residual Elements from Steel Scrap at the Iron and Steel Institute of Japan (ISIJ), composed of 23 members, carried out fundamental research on feasible methods for removing residual elements from steel scrap for five years from May 1991 to February 1996.1) The Japan Research and Development Center for Metals (JRCM), subsidized by the Ministry of International Trade and Industry (MITI), has been conducting a 13-company joint research project for eight years from 1991 to 1998 to study the practical process of scrap based steelmaking process.2)

This report describes the activities of the above two research groups on the technology for removing the residual elements copper and tin from steel scrap.

2. Adverse Effects of Copper and Tin on Steel and Targets for Their Removalfrom Steel Scrap

Whether or not residual elements pose a practical problem depends on the minimum contents at which they start to exert an adverse effect on the quality of steel and the actual contents at which they are contained in steel scrap. Table 1 shows the adverse effects of the residual elements on steel and the contents of the residual elements in present steel scrap. Of the residual elements, copper and tin are the ones to adversely affect the hot workability of steel.

The acceptable levels of copper and tin for typical steels are shown in Table 2. Examples of scrap compositions are given in Table 3. The residual element problem does not surface as long as steel scrap is used for making shapes, bars and other steel products that have lenient residual element restrictions. Such situation has been maintained until the obsolete scrap accounted for 30% or less of all ferrous raw material.

In Japan, the generation of obsolete scrap began to increase in 1995 when the total steel production plateaued, and the generation of obsolete scrap is predicted to exceed 40% of total steel production in 2010 (Fig. 1). In that case, the steel scrap generation will surpass the demand unless steel scrap is used to make steel products other than shapes and bars; for example, sheets.

One solution is such an improvement in hot workability as to increase the permissible limits of copper and tin in steel. This has been studied by many investigators. To use all of scrap generated while meeting the present impurities allowance, the authors studied:

(1) To what level copper and tin must be removed from steel scrap.

(2) How copper and tin should be removed to meet the removal target.

The results of subject (1) studied under several assumptions (see Appendix) are shown in Fig. 2.3) To summarize, copper and tin will have to be removed by 55% and 30%, respectively, from steel scrap in 2010.

Table 1. Effect of residual elements in scrap recycling

Element	Adverse effect on quality of steel	Present content in scrap	Urgency of removal
Cu	Adversely affects hot workability at content of about 0.2%	0.1~0.3%	Immediate removal required
Sn	· Adversely affects hot workability at content of about 0.04% · Adversely affects cold workability and temper brittleness at content about 0.2%	0.005~0.016%	Removal required depending on tin can recycle
Ni	· Increase hardness and objectional for sheet product	0.06~0.1%	Removal required in future
Cr	· ibid. · Adversely affects cold workability	0.03~0.3%	ibid.
Zn	· Forms white smoke during iron casting	Removal content of 0.005% of less in steel	Dust treatment required
Pb	· Adversely affects hot workability at content of 0.001%	—	ibid.
As	· Adversely affects hot workability at content of 0.03% · Adversely attects cold workability and temper brittleness at content of 0.02%	Details not known	Removal required in future
Bi	· adversely affects hot workability at content of 0.005%	ibid.	

Table 2. Examples of allowance of copper and tin (mass %)

Steel grade	Cu	Sn
Deep draw quality plate	≦0.60	≦0.010
Hot or cold rolled sheet	≦0.10	≦0.020
Shape	≦0.30	≦0.025
Bar	≦0.40	≦0.060

3. Methods for Removing Copper from Steel Scrap

Copper may be present in steel scrap in two forms:

(a) Copper physically mixed with steel (for example, motor cores)

(b) Copper dissolved in steel

Once elements like copper and tin which are more noble than iron are dissolved in iron, they are difficult to be removed from iron. The authors laid emphasis on removing copper from iron when copper is present in a separate phase from iron. Since it is sometimes necessary to reduce

Table 3. Examples of composition of various grade of scrap (mass %).

Grade		Cu	Sn	Cr	Ni	Pb	Zn
Heavy	HS	0.13	0.012	0.05	0.08	—	—
	H1	0.09	0.003	0.07	—	—	—
	H2	0.24	0.018	0.10	0.10	—	—
	H3	0.33	0.015	0.19	—	—	—
Pressed	A pressed	0.64	—	0.03	0.11	—	—
	C pressed	0.64	0.40	0.05	0.06	—	—
	New punched	0.04	—	0.04	0.02	—	—
Shredded		0.23	0.01	0.28	0.07	0.026	0.22
Turnings		0.19	—	0.27	0.09	—	—

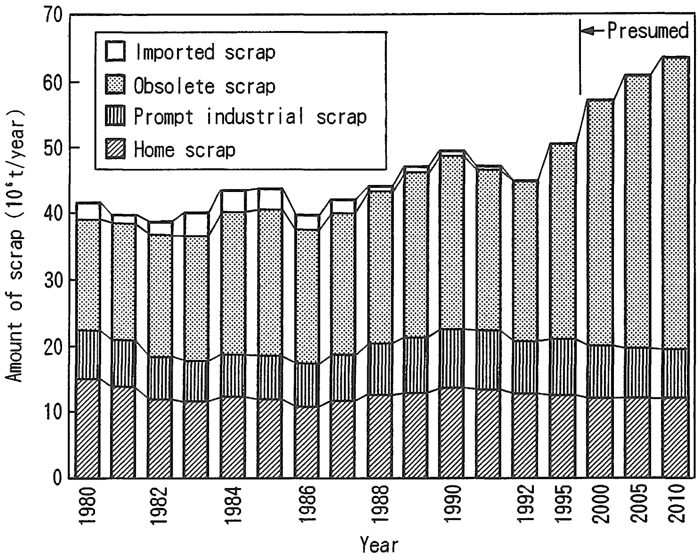

Fig. 1. Generation of various scrap in Japan.

the copper content of molten steel, the removal of copper from molten iron was also studied.

(1) Methods for separating copper from iron in different phases

(i) Mechanical separation (Fig. 3)

When discarded automobile scrap is processed by conventional shredding, the content of residual copper in the resultant steel scrap is about 0.2%. The residual copper content can be reduced to 0.15 to 0.12% by shredding the steel scrap repeatedly or manually sorting the steel scrap. When the steel scrap is cooled to − 100°C or lower with coolant such as liquid nitrogen,

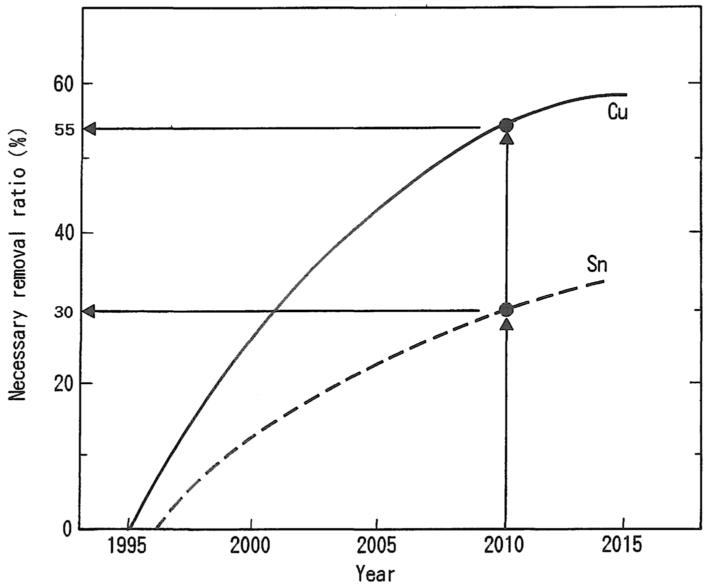

Fig. 2. Calculated necessary removal ratio of copper and tin to use all steel scrap generated in 2010.

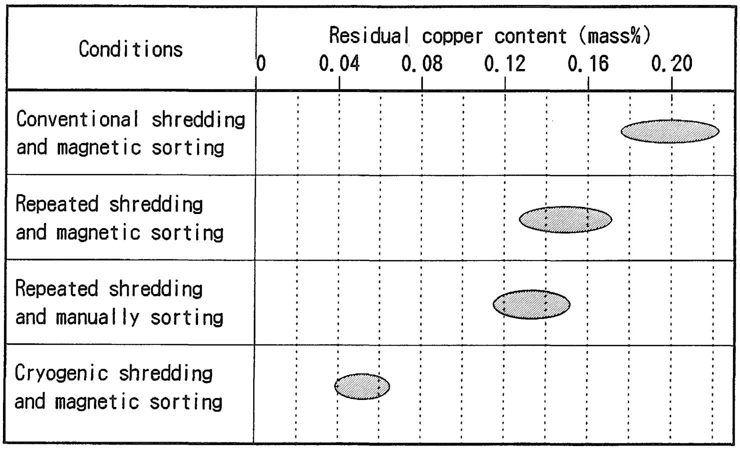

Fig. 3. Influence of conditions of shredding and sorting on residual copper content in steel scrap. (Discarded automobile scrap)

followed by being shredded and magnetically separated, the residual copper content may be lowered to 0.04 to 0.06%. The iron content of scrap separated as copper rich fraction can be kept as low as 10% or less. If the separated copper fraction is to be used in the copper refining process, the iron content should be as low as possible. The addition of cryogenic processing has the benefits of lowering the content of residual copper in scrap, and improving the recyclability of recovered copper.

Cryogenic processing has the disadvantages of additional cost of liquid nitrogen for 500 to 1,000 kg of liquid nitrogen required to cryogenically process for one ton of scrap and small scrap piece size of 10 mm or less. Cryogenic processing may be applied not to entire automobile scrap but to shredded copper-rich pieces like those of motor cores.

A color image analysis was developed for precisely separating shredded pieces which are likely to contain copper from the rest of the shredded material.

A test using copper-bearing motor core pieces has resulted in 100% separation (Table 4).

(ii) Recovery of copper as alloy by melting in molten metal bath

Copper is melted and separated in such a temperature region that iron is not melted. The metal bath to be employed for this purpose may be molten aluminum4), lead5) or magnesium6). The aluminum bath is most practical among the three types of metal baths studied because it is easy to handle and because copper can be readily separated from aluminum7). Like the cryogenic processing described in (i) above, this melting mothod is considered to be more effective when applied to sorted pieces of scrap like motor cores rather than to the entire scrap stream.

(iii) Chloridization and vaporization of copper

The basic problem to be solved to accomplish this method is how to prevent coexisting iron from vaporizing as chloride. This problem can be overcome by adjusting the partial pressure of oxygen and chlorine in the furnace atmosphere and turning copper into chloride while covering iron with an oxide film as shown in Fig. 4.8) It is known that copper can be separated in a chlorine-oxygen mixed gas atmosphere in the laboratory. Practical application of this method calls for protection of apparatus against corrosion and treatment of waste gas, among other things.

(iv) Removal of copper by utilization of melting temperature difference between copper and iron

Already in the late 1960s, the Bureau of Mines of the United States tried to melt and remove copper from motor cores by heating them to temperatures above the melting point of copper.9). The copper removal ratio significantly depends on heating conditions. Considering that the wettability of scrap by copper droplets is influenced by the properties of the oxide film formed on

Table 4. An example of experimental result of scrap separation by a color image analysis (Number)

	Sample	After separation	
		Copper rich fraction	Copper less fraction
Motor cores	5	5	0
Steel scrap without copper	95	5	90

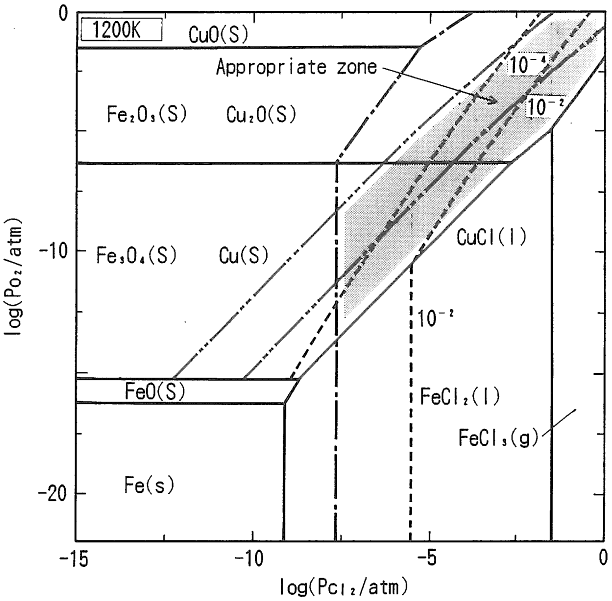

Fig. 4. Phase diagram of Fe-Cu-Cl-O and appropriate condition for vaporization of copper from motor core.

the scrap, Hara conduced a fundamental study. An oxide film was formed on silicon steel, by changing the partial pressure of oxygen in the gas phase at 1,373 K and the angle of contact with molten copper in equilibrium with the gas phase was measured.[10] The work of adhesion, Wad was calculated from the measured angle of contact, θ and the surface tension, γ of the liquid phase by

$$Wad = \gamma (1 + \cos \theta) \quad (1)$$

The relationship between the work of adhesion and the composition of the atmosphere is shown in Fig. 5. When the work of adhesion is small, the copper is easily separated from the iron when:

(a) The oxide film is composed of SiO_2 or $2FeO \cdot SiO_2$ (region A); or

(b) Magnetite, not wustite, is formed (region C).

In the region where wustite is formed, the oxide film is so weak that some of the molten copper reaches the steel base through the oxide film. This is considered as the reason why the work of adhesion is increased in the region B where wustite is formed.

The removal of molten copper depends on the shape of scrap. A high copper removal ratio is difficult to be obtained by this method on a constant basis, but residual content of scrap may be reduced to some extent as a secondary benefit of scrap preheating.

(v) Selective dissolution of copper by wet process

Motor cores were immersed in a variety of solutions, including those of amine ions (such as ammonia solution[11] and thiocyanate solution[12]), concentrated nitric acid[13] and sulfuric acid[14]. The solutions were compared in terms of dissolution selectivity and rate of copper. When combined

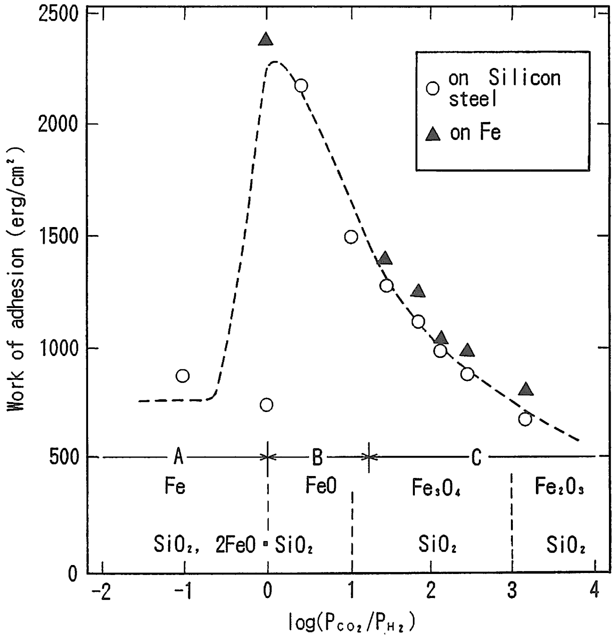

Fig. 5. Work of adhesion, W_{ad} molten Cu on steel plate as a function of P_{co2}/P_{H2} at 1373 K.

with oxygen blowing, an amine ion solution can selectively dissolve the copper with the greatest stability and at a relatively high rate. The sulfuric acid solution can also dissolve the copper at a relatively high rate, but involves the problem of passive film breakage due to reaction-induced local nitric acid concentration drop. A small-sized experiment confirmed that the application of voltage is effective in preventing this problem. The sulfuric acid solution dissolves the copper at a rate lower than that of the nitric acid solution, and its selective copper dissolution is inferior to that of the amine ion solution.

Before dissolving copper, motor cores must be heated for removing enamel coating on copper wire.

(2) Methods for removal of copper dissolved in iron

(i) Method for treating with sulfide flux

Sulfide has been long known as a flux for removing copper dissolved in iron.[15] Copper distribution ratios were determined using various fluxes.[16,17] As shown in Fig. 6, the copper distribution ratio under optimum conditions is 30 at most and usually about 20 when Na_2S based fluxes are used.

To achieve a high copper removal rate with this degree of distribution ratio, a large amount of flux is required. To remove copper by 50%, for example, at least 75 kg of flux is required per ton of scrap. The flux must be stabilized and should be recycled if possible. Fundamental experiments confirmed that the flux can be recovered as Na_2S or Na_2SO_4 from the water solution from

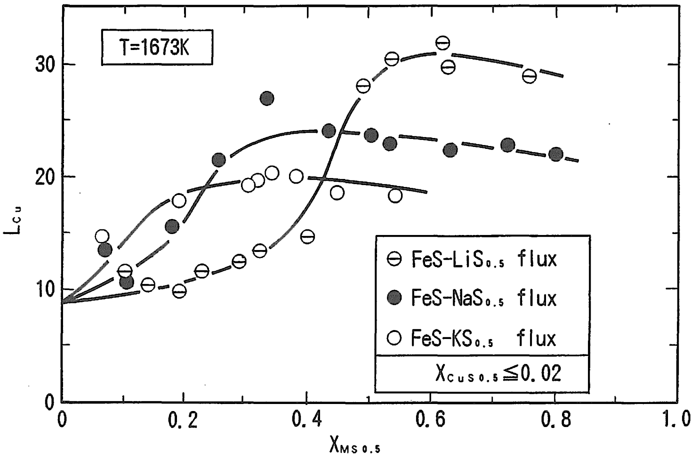

Fig. 6. Effect of alkaline metal sulfide, $MS_{0.5}$ in FeS-$MS_{0.5}$ fluxes on L_{Cu} at 1673 K.

which the sodium constituent is leached with water.[18]

(ii) Method for promoting vaporization of copper

The rate of removal by vaporization of copper from molten iron depends on the pressure (Fig. 7) and the activation energy is 160 to 230 kJ/mol.[19]

To achieve a copper removal ratio of 50% or more by treating a large volume of molten steel, it is necessary to provide a far larger specific surface area than in the ordinary process. One idea conceived involves oxidizing a carbon-containing steel bath, forming CO bubbles, and accelerating

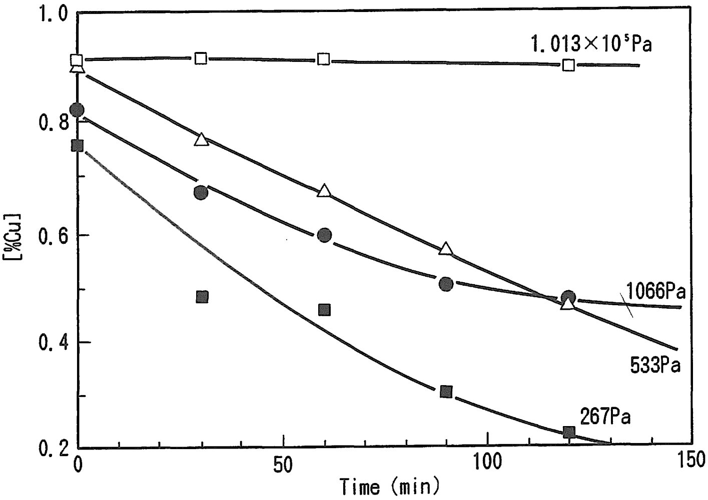

Fig. 7. Effect of pressure on copper removal from iron melt at 1773 K.

the vaporization of copper from the metal bath. A 1-ton experiment was conducted to verify the validity of this approach (Fig. 8). Of various oxidizing agents, those with low oxidizing capacity like SiO_2 were most effective.[20)]

It is confirmed by the results of a 20-kg experiment that the rate of copper separation from molten steel can be increased by blowing ammonia into the molten steel under vacuum.[21)] The extensive generation of splash in this case suggests that an activated gas (hydrogen or nitrogen) is dissolved in the molten steel and that when it is released from the molten steel at other sites, the resultant bubbles increase the specific surface area of the molten steel.

(3) Evaluation of Methods from the Practical Point of View

Mechanical separation and sorting by shredding will remain a predominant practical method for the time being. It is hoped that sorting of shredded motor cores will advance in automation to such a degree that copper-containing pieces will be properly separated from the rest of shredded scrap. The separated copper-containing pieces will be concentrated in copper by cryogenic shredding, aluminum bath immersion or amine ion solution dissolution so that the copper can be efficiently recovered (in the copper refining process, for example).

When steel scrap is preheated, cooper-containing pieces may be separated to some degree by making use of difference in melting point if the partial pressure of oxygen in the atmosphere is adjusted to a proper level, for instance.

If it is necessary to reduce the copper concentration in the molten steel bath, some degree of copper removal can be accomplished by increasing the specific surface area of the bath by utilizing

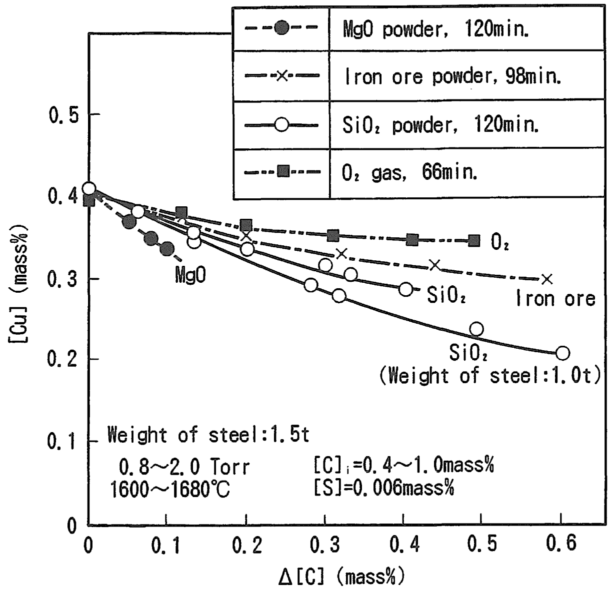

Fig. 8. Effect of oxidizing agent on removal of copper.

the evolution of bubbles from the bath.

The above methods may be used in combination in order to acconplish the target copper removal ratio of 55% on average.

4. Method for Removing Tin from Steel Scrap

Tin exists in steel scrap in two forms:

(a) Tin contained in the tin coating

(b) Tin dissolved in steel.

The methods that can remove tin from steel scrap in principle are summarized in Table 5.

The tin content in steel scrap is about one magnitude smaller than copper, so that it is not as advantageous to recover it from steel scrap as copper. Furthermore, tin coating thickness has been diminishing in recent years. The addition of a process only for removing tin from steel scrap is not economically warranted. For example, the method of separating tin coatings from steel scrap by electrolysis is already established technically, but is not commercialized due to high electric power cost in Japan.

Each of the methods listed in Table 5 is feasible in principle. The methods that use sulfur[22], chlorine or chloride gas[8,23] to treat steel scrap to remove tin call for special processing and are not practicable enough. When tin is vaporized as primary element by treating molten steel under vacuum, its vaporization rate is equal to or lower than that of copper[19], so that special vacuum treatment conditions as described for copper are required.

The following two methods have been studied to remove tin from steel scrap as a secondary benefit in the steel scrap preheating and melting steps:

(i) Method for oxidizing surface of tin coating and removing oxidized tin coating in the steel scrap preheating step[24]

Assuming the use of a rotary furnace for preheating steel scrap, this method is designed to

Table 5. Feasible methods for removing tin from steel scrap.

Form of tin in steel scrap	Principle of removal		Operation temperature
Tin in coating of steel	① Removal of tin by electrolysis		≦50°C
	② Peeling of tin coating	Formation of Brittle sulfide	~500°C
		Formation of scale	~950°C
	③ Vaporization of tin as chloride		150~300°C
Tin dissolved in steel	④ Vaporization of tin by converting into sulfide of suboxide		1500~2500°C (at hot spot) (during melting at normal pressure)
	⑤ Vaporization of elementary tin		1600~1680°C (by advanced vacuum treatment)

oxidize and remove the tin coating from steel scrap. Two kilograms of scrap was charged in a 35 cm diameter, 50 cm long stainless steel reactor pipe heated to 950°C, and rotated. The experimental results are given in Fig. 9. Tin was removed by about 20% from the steel scrap under this method. When the charge was rotated together with tungsten balls of high specific gravity in the reactor pipe, the increased impact force applied to the charge doubled the tin removal ratio to 40%.

When steel scrap was heated to about 500°C in a sulfur-containing atmosphere in a separate experiment, the coated tin was changed to brittle stannous sulfide (SnS) and peeled off. As a result, the tin removal efficiency was 70% or more for tinplate and about 40% for tin cans.[22] But the use of the sulfur-containing atmosphere gives rise to such problems as the need for special atmosphere control and the penetration of sulfur into the scrap surface.

(ii) Method for vaporizing tin as SnS in scrap melting step[25]

Steel scrap may be heated and molten electrically as well as by the combustion of fossil fuel like coke or coal with oxygen blowing. In the latter case, tin is vaporized prior to iron under special conditions and concentrated in the dust emitted from the process.

The necessary condition to be met for the method is the isolation of an oxygen gas jet from a stirred molten iron bath by a thick slag layer (Fig. 10). Under this condition, the generation of iron dust by bubbles bursting is suppressed, even if the carbon concentration is high in the iron bath. At the same time, the tin forms stannous sulfide (SnS) with the sulfur contained in the fossil fuel (the sulfur content of the metal may be 0.1% or less), and its vaporization is accelerated by the high temperature (estimated at 2,500°C or more) of the oxygen-blown hot spot. As a result, the tin is concentrated in the dust emitted from the furnace.

If the tin separation capacity is expressed by the tin consentration ratio: α_{Sn}, it is given by

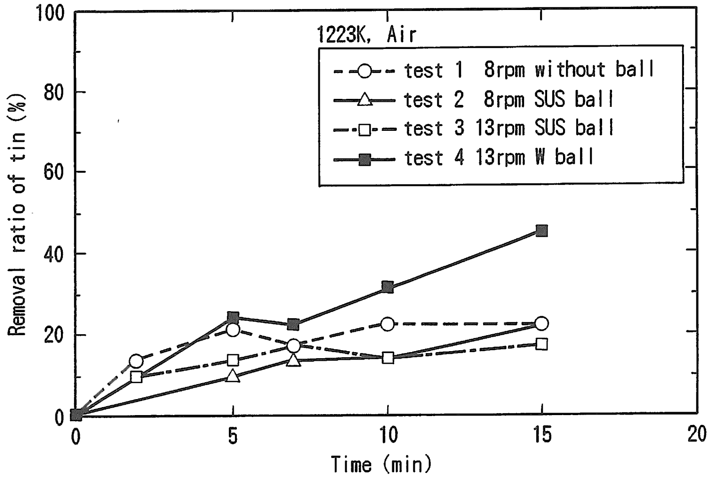

Fig. 9. Influence of rotary condition of reactor pipe on removal of tin.

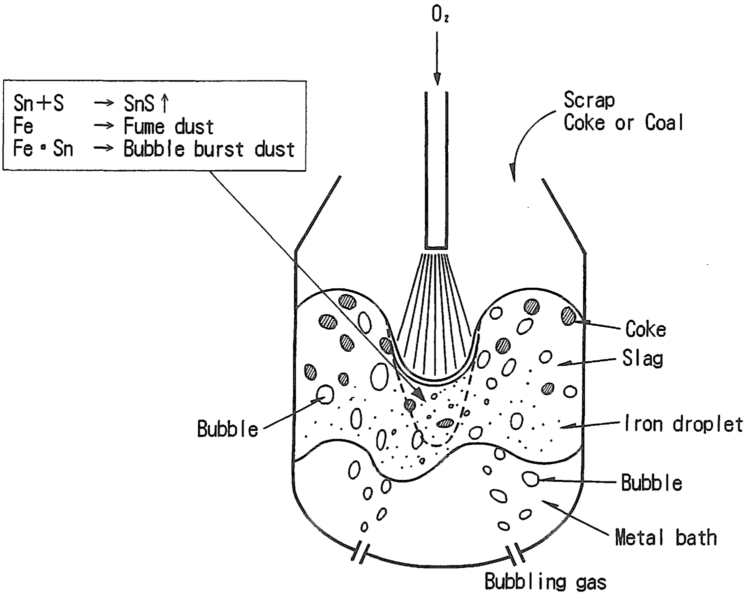

Fig. 10. Shematic drawing of scrap melting for accelerating removal of tin to dust.

$$\alpha_{\mathrm{Sn}}=\frac{\text{Tin/iron concentration ratio in dust}}{\text{Tin/iron concentration ratio in metal bath}} \tag{2}$$

A value of about 20 was experimentally obtained under optimum conditions (Fig. 11). α_{Sn} rises further if tin-coated steel scrap is used.

Tin removal efficiency; β_{Sn} is given by

$$\beta_{\mathrm{Sn}}=\frac{\text{Tin output to dust}}{\text{Tin input}}\times 100\ (\%) \tag{3}$$

The relationship between $\alpha_{\mathrm{Sn}}$and β_{Sn} is expressed as Fig. 12. As iron dust loss is ordinary about 3%, the tin removal ratio; β_{Sn} in this process if 35%~60%.

5. Total System for Removing Residual Elements from Steel Scrap

A total scrap melting system faces such challenges as minimizing the melting energy requirement and rendering dust and waste gas harmless as well as removing copper and tin as discussed above.

The total system under consideration now is conceptually illustrated in Fig. 13.

How to treat dust and other products containing zinc, lead and tin, among other residual elements, and how to recover them as valuable metals economically are issues to be studied further.

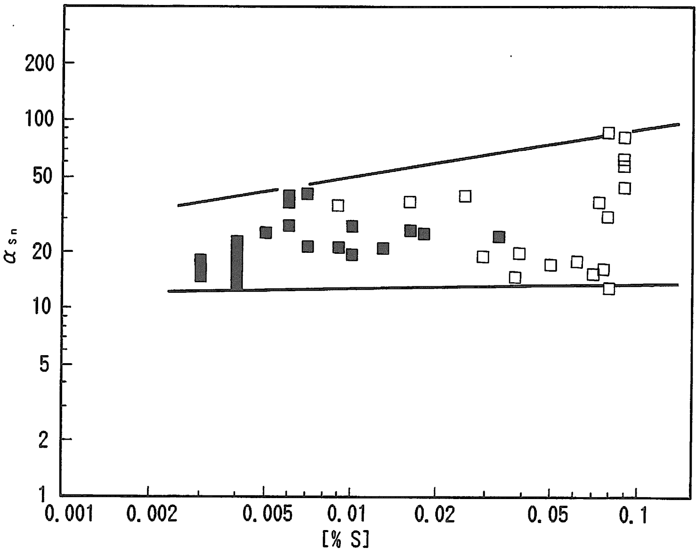

Fig. 11. Influence of [% S] on α_{Sn} in Eq. (2). (Different plot means different heat.)

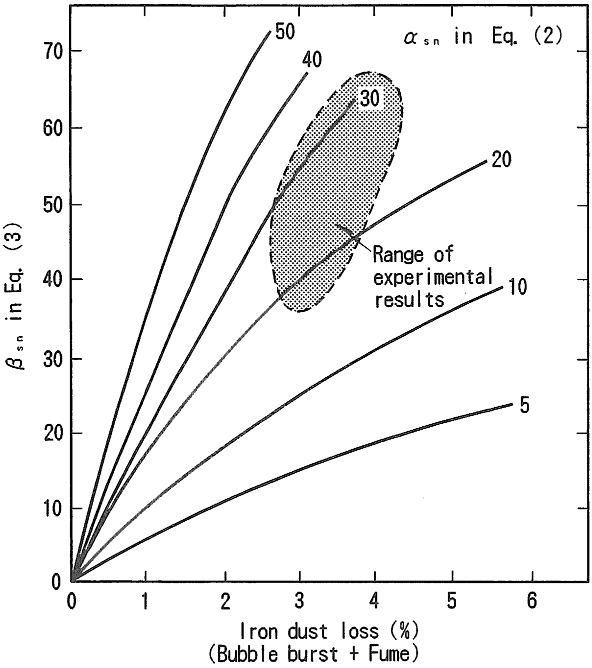

Fig. 12. The relationship among dust loss ratio, tin concentration ratio (α_{Sn}) and tin removal ratio (β_{Sn})

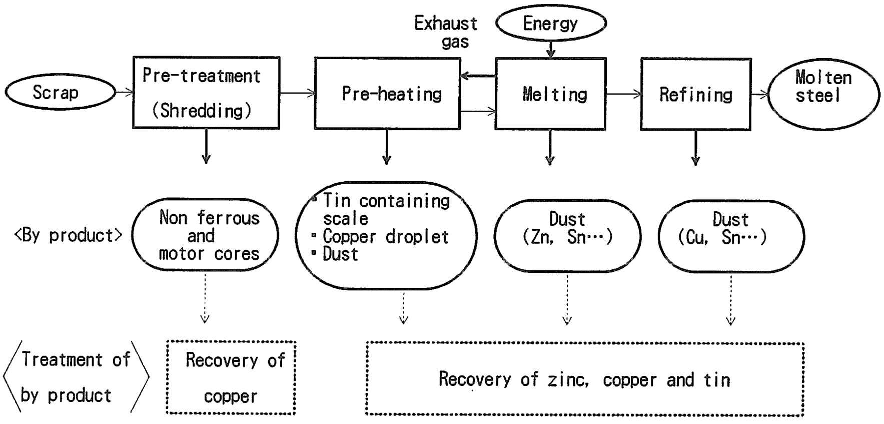

Fig. 13. Total system for processing steel scrap.

6. Summary

This paper has outlined the activities of two Japanese research groups (Committee for Removing Residual Elements from Steel Scrap of the Iron and Steel Institute of Japan and Scrap Recycle Technology Project of the Japan Research and Development Center for Metals (JRCM)) on the removal of copper and tin from steel scrap.

To use all of steel scrap generated as feed material for steel production in 2010, copper will have to be removed from steel scrap by about 55% on average. Of the methods feasible in principle for removing copper from steel scrap, combination of conventional shredding followed by automatic sorting and treatment of copper rich fraction by cryogenic shredding and magnetic separation, aluminum bath immersion or wet treatment with ammonia are expected to find early commercial applications.

The necessary average removal ratio of tin is about 30%. To accomplish this target, research was conducted not to add another process, but to remove tin from steel scrap as secondary benefits of steel scrap preheating and melting steps operated under optimum conditions. As a result, two methods were found to be promising for removing tin from steel scrap. One method is to oxidize and remove tin when the steel scrap is preheated, and the other is to vaporize tin as stannous sulfur (SnS) when the steel scrap is melted by oxygen and coke or coal.

A total scrap melting system with the addition of copper and tin removal from steel scrap or molten steel will be evaluated in the JRCM project.

Appendix

Assumptions for calculating necessary average removal ratio of residual elements as required to reuse all of steel scrap generated

(i) Crude steel production: Same as current level (100 million tons per year).

(ii) Types and composition of steel scrap: Steel scrap is divided into low-grade scrap (heavy scrap and shredded scrap) and high-grade scrap (punchings and trimmings), and pig iron is used for dilution.

(iii) Generation of steel scrap: Of iron and steel stock, 2.7% becomes obsolete scrap, and no steel scrap is exported.

(iv) Increase of copper concentration in steel scrap: 2.5% per year.

(v) Increase of tin concentration in steel scrap: 0.75% per year.

(vi) Steel product quality: Same as current level.

References

1) Committee for Removing Residual Elements from Steel Scrap; 'Fundamental Study on the Removing Residual Elements from Steel Scrap', (1996), p. 3, ISIJ.
2) S. Sato, M. Takeuchi, Y. Mizukami and J. P. Birat; La Revue de Mettllurgie-CIT Avril (1996), p. 473.
3) JRCM NEWS, No. 100 (1995. Feb.).
4) M. Iwase and K. Tokinori; Steel Research, 62 (1991) p. 235.
5) K. Mori; Same as reference 1). p. 93.
6) Hiroshi Katayama; ibid., p. 97.
7) M. Iwase; ibid., p. 101.
8) K. Nagata; ibid., p. 83.
9) R. B. Brown, F. E. Block; U. S. Bureau of Mines, Report of Invest. 7218 (1968).
10) S. Hara; Same as reference 1), p. 105.
11) K. Shinme, S. Anezaki; J. of MMIJ, 111 (1995) 1, p. 49.
12) T. Yamashita; Same as reference 1), p. 115.
13) K. Nagata; ibid., p. 125.
14) T, Nakamura; ibid., p. 119.
15) F. C. Langenberg, R. W. Rindsay and D. P. Robertson; Blast Furnace Steel Plant, 43 (1955), p. 1142.
16) T. Imai, N. Sano: Tetsu-to-Hagane, 74 (1988), p. 640.
17) O. Cho, J, Hirama, T. Nagasaka, S, Banya; Tetsu-to-Hagane, 77 (1991), p. 353.
18) T, Nakamura; Same as reference 1), p. 77.
19) K. Mori; ibid., p. 19.
20) T. Matsuo, K. Maya, T. Nishi, K. Shinme, A, Ueno and S. Anezaki: ibid., p. 29.
21) K. Ono and E. Ichise; CAMP-ISIJ(1994). p. 1143.
22) K. Ounuki and T. Tokumitsu; CAMP-ISIJ(1996), p. 807.
23) A. D. Hartman, L. L. Oden and D. L. Davis: I & SM, May (1994), p. 59.
24) K. Ogawa and H. Matsumoto; CAMP-ISIJ (1996), p. 806.
25) H. Katayama. H. Hirata and Y. Demoto; Reference 1), p. 37.