Copper and Tin in Steel Scrap Recycling

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Abstract: Copper is the key element related to surface defects of steel caused by a loss of ductility in the temperature range of 1050-1200 °C. Tin increases the negative effect of copper. The main source of copper and tin in the steelmaking is obsolete scrap. The possibilities and limits of contaminated steel scrap recycling and methods of scrap purification are discussed.

Key words: steelmaking, scrap recycling, scrap purification, copper, tin, tramp elements

1 COPPER AND TIN IN THE STEEL CIRCUIT

1.1 Effect of copper and tin on steel service properties

Copper and tin are harmful tramp elements in steels. They can directly influence the mechanical properties of steel products. Copper contributes generally to an increase in corrosion resistance and mechanical strength associated with a ductility loss of steels. Copper is the key element related to hot shortness caused by a loss of ductility in the temperature range from 1100 to 1300 °C. Surface defects can appear along the whole hot processing line, during casting or hot rolling (Figure 1).

It can be seen that hot cracks begin to form at copper contents above 0.2 % [1] where the crack depth is a function of copper content in the steel. The crack depth increases with increased copper content.

Alloying and tramp elements in steel, especially tin, modify the negative effect of copper [2]. This interaction between alloying and tramp elements is considered a synergism effect. Some elements amplify while others neutralise the negative effect of copper. This effect can be illustrated by empirical expressions for the so-called “copper equivalent” (Figure 1). From this equivalent it is concluded, that elements such as antimony, tin and arsenic when present in steel increase the harmful effect of copper while the presence of nickel reduced it. 0.4 % of copper in steel exerts the same negative influence on the steel product properties as the sum of (0.3 % Cu + 0.02 % Sn). Due to this synergism effect, the tramp elements copper and tin must be considered together. The tolerable contents of copper and tin are fixed by standards for different steel qualities. Whereas the maximum content of copper in bar steel is 0.4 %, that of cold-rolled sheet is only 0.04 % (Figure 1). In the course of casting and hot rolling not only copper and tin content in steel must be fixed, but also the sum of all
Impurity element copper
Other metallic impurities: Sn, Zn, Pb, Sb, As, (Cr, Ni, Mo)

Effect of Cu on steel properties: mechanical strength, corrosion resistance
toughness
Interaction between Cu and Sn, synergism effects
0,4% Cu in steel exert the same influence as 0,3%Cu+0,02%Sn
Copper equivalent =%Cu+(10%Sb)+(5%Sn)+(2%As) - %Ni

Tolerable contents of Cu and Sn, in %
<table>
<thead>
<tr>
<th>steel grade</th>
<th>Cu, %</th>
<th>Sn, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>bar steel</td>
<td>max. 0,40</td>
<td>max. 0,06</td>
</tr>
<tr>
<td>cold-rolled sheet</td>
<td>max. 0,04</td>
<td>Max. 0,02</td>
</tr>
</tbody>
</table>

bar steel $\Sigma(%Cu+%Cr+\%Ni+\%Mo)$=max. 0,13%
thin sheet $\Sigma(%Cu+%Cr+\%Ni+\%Mo)$=max. 0,80%

Figure 1. Copper problems in steelmaking

tramp element contents has to be considered. For example, the sum of copper, chromium, molybdenum and nickel contents is controlled.

1.2 Main sources of copper and tin

Copper and tin are introduced to steel using steel scrap in the steelmaking process (Figure 2). Generally, steel scrap is divided into the three categories:
- home scrap from steelmaking and rolling mills,
- process scrap from steel processing lines,
- obsolete scrap from consumer goods.

Obsolete scrap consists of iron or steel products discarded after the end of their service life. Post-consumer steel products include old passenger cars, steel cans, electric appliances and other items. Obsolete scrap is often mixed or coated with other materials, such as copper, tin, glass and polymers. For this reason the content of tramp elements in obsolete scrap is usually high and this scrap is a main source of copper and tin in steelmaking processes. Obsolete scrap is usually processed by shredding. Thereby the scrap is crushed and the steel parts are separated from the other nonferrous parts. In spite of crushing, a mix of steel and copper parts exists. This is the main cause for the fact that non-magnetic copper remains in the magnetic, iron-rich fraction.
Scrap from higher copper containing steels such as concrete reinforcing steels or stainless steels, is a second main source of copper in steelmaking. Copper appears in this scrap in the dissolved state. Tin is supplied by tinplate from beverage and food cans and other packages. Tinplate is a cold-rolled steel plate coated with a thin layer of tin. 2 to 8 kg pure tin is used for the coating of 1t steel plate depending on the thickness of steel plate and tin layer. This means that the steel melt can contain 0.2 to 0.8% tin after the smelting of the tinplate scrap. In Germany, the largest amount of tinplate scrap is obtained by separation from household refuse. The average tin content in the refuse of separation scrap is 0.3 % \(^3\).

| Scrap grades       | • Home scrap (from steelmaking and rolling mills)  
|                   | • Process scrap (from steel processing industries)  
|                   | • Obsolete scrap from consumer goods (world-wide share 60%)  
| Copper sources     | • Shredder scrap from used cars and household white ware. Copper parts mixed with steel components (e.g. small electric motors)  
|                   | • Scrap from higher Cu-containing steels (constructional and corrosion-resistant steels) Copper in solid solution with steel  
| Tin sources        | • Tin plate scrap from beverage and food cans and other packages. Tin as a metallic coating. 2 to 8kg of Sn used for the coating of 1t steel sheet. 0.3% of average Sn content in refuse separation scrap  

**Figure 2.** Main sources of the steel impurities copper and tin
1.3 Appearance of copper and tin in charge materials, steel scrap and steelmaking dust

The main impurity contents in steel charge materials of Voest-Alpine Linz AG are shown in (Figure 3) \cite{4}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Main impurity contents in charge materials Voest-Alpine Linz AG (oxygen steel plant) \cite{4}.}
\end{figure}

Copper impurities coming with the \textbf{hot metal} can be neglected. But the copper impurities from shredder and obsolete scrap are remarkably high.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Copper impurities of steel scrap in Japan 1996 \cite{5}.}
\end{figure}
A Japanese study deals with steel scrap pollution by tramp elements \cite{5}. The samples from the scrap were taken nationwide in Japan. Copper, tin and chromium contents in the scrap samples were controlled. The frequencies of the measured copper contents are given in Figure 4. The average copper content in the steel scrap is 0.297%.

**Dust** emissions in steelmaking processes exhibit higher levels of tin and other heavy metals contained in the zinc coating \cite{6}. The tin content of EAF dusts is not sufficient to ensure economically viable recovery. On the other hand, increased levels of tin in the BOF dust make their usual recycling via the sinter plant/blast furnace route problematic because of the harmful effects of zinc in the blast furnace. In steelmaking practice, it was established that in contrast to tin and lead no essential copper upgrading occurs in the steelmaking dust.

Copper and tin are not found in steelmaking slag. The melting temperatures of pure copper and tin are much lower in comparison with steel (1083 °C for copper and 232 °C for tin), Figure 5. At typical steelmaking temperatures, around or above 1600 °C, the solubilities of copper and tin in the steel melt are practically unlimited.

In comparison with iron, copper and tin are characterized by a lower oxygen affinity. Accordingly, they are not removed by oxidation and transferred to the slag. It is therefore understood, that copper and tin stood appear only in the steel.

<table>
<thead>
<tr>
<th>Melting temperature</th>
<th>Cu 1083°C</th>
<th>Sn 232°C</th>
</tr>
</thead>
</table>

**Solubility** of Cu and Sn in steel around 1600°C is practically unlimited

**Oxygen affinity** of Cu and Sn is lower than that of iron

**Consequences**
- Cu and Sn dissolved in molten steel cannot be removed by oxidative refining
- Slags in steelmaking are practically free of Cu and Sn

![Figure 5. Behaviour of copper and tin in steelmaking processes.](image)

\[ \text{partition coefficient} = \frac{\%X_{\text{in steelmaking dust}}}{\%X_{\text{in steel}}} \]
2 ENRICHMENT OF COPPER AND TIN IN STEELMAKING PROCESSES

2.1 Development of scrap quality

The development and forecast of scrap quality standards is given in Figure 6 for the period 1985-2015 [6]. During this period the amount of home scrap is falling, but no changes of the processing scrap occur. On the other hand, the obsolete scrap, which is the main source of the tramp elements' increases. The development in the automobile industry is the cause for the increasing copper contents in the obsolete scrap. There exists a tendency to employ more electric motors and copper holding electronic elements in the cars. Due to the miniaturization of these parts, they are difficult to crush and to sort by shredding, with the result of increasing copper contents in the scrap, which are accumulated. In the steel and lead to a regular copper upgrading in the steel circle. Tin content in the steel circle increases at the same time. This is caused by increasing recycling rates of tin-plate packages. The development of material flow is schematically shown in Figure 7. The copper and tin contents are given as dark-grey areas.

Scrap  home scrap  processing scrap  obsolete scrap

Cu content in obsolete scrap
(mainly caused by developments in car construction)

Sn content in obsolete scrap
(caused by increasing recycling rates of tin-plate packages)

Cu and Sn charges are steadily increased by steel scrap impurities

Figure 6. Development of scrap quality standards [6].
2.2 NEED FOR COPPER AND TIN REMOVAL

The developments in steel making and non-ferrous metal making are illustrated in Figure 8.

The steel industry has always aimed at a higher steel yield through rationalisation of equipment and technology. The customer demands for improved steel service properties require lower impurity levels. On the other hand, the incoming scraps feature increased impurity levels, so that the steel-makers face the difficult task to produce steels with lower tramp element contents from higher tramp element holding scraps.

Thus copper and tin removal from scrap by pre-treatment is desirable. With the following benefits to be aimed at:

- use of contaminated, low-cost steel scraps to produce higher steel grades,
- avoidance of dumping of higher copper and tin containing scraps as waste materials,
- support of a sustainable strategy to integrate contaminated steel scrap into a secondary material circuit of the metals copper and tin.
## Developments in Steelmaking

| Increasing demands with respect to steel service properties | Lower impurity levels required |
| Increasing impurity levels in steel scrap | Not acceptable for higher steel grades |
| | Possibly applicable for lower steel grades |

## Developments in nonferrous (NF) metal economy

| Copper withdrawn from NF metal industrial circuit | Copper recycling rate reduced |
| Tin withdrawn from NF metal industrial circuit | Tin recycling rate reduced |

*Figure 8. Developments in steel making and nonferrous (NF) metal making economy.*

### 3 Proposed methods for scrap and melt purification

#### 3.1 Suggested methods

Copper and tin dissolved in steel melts are not oxidised in the presence of iron due to their lower affinity for oxygen. This means that these elements cannot be removed from a steel scrap melt in a common pyrometallurgical process, as is the case with aluminium, i.e., which is easily oxidised and dissolved in the slag. In order to remove tramp elements from scrap, there exist essentially two different pre-treatment routes (Figure 9). Mechanical separation belongs to the first route. The second route encompasses the chemical and metallurgical removal methods. The main advantage of metallurgical separation consists in the fact that the tramp elements can be removed independent of the their appearing form in the scrap, e.g., as segregations coatings or in the dissolved state.

For the treatment of molten steel several procedures were suggested and tested on an experimental scale:

- treatment by reaction with sulphur-containing slag,
- vacuum distillation and
- other treatment methods.
3.2 Steel scrap pre-treatment

Laboratory-scale tests of scrap pre-treatment to remove copper are explained in Figure 10. In the separation method by smelting of copper parts from a mix with solid steel (1), the difference in the melting temperatures of the impurity elements and the steel is used. The pre-melted copper is separated by liquid flow and is collected while the steel parts remain in the solid state. This method was investigated and realised for automobile scrap and scrap from electromotors in the USA [7, 8] with the result that the copper removal rate was insufficient. Through oxidation, some copper was enclosed in the iron oxide. Under reduced conditions, the alloying of the liquid copper with the steel was increased.

In Japan, the flow-off of copper droplets from the steel surface as a function of the oxygen partial pressure has been investigated [9]. Copper easily flows down the magnetite and iron-silica surfaces, but the adherence between copper droplets and wustite is remarkably high.

The disadvantages of the separation by smelting of copper parts are due to a low separation rate, which is caused by copper losses (for example flow of copper into cavities) and steel losses caused by oxidation and are particularly due to the remarkable fuel costs. On the other hand, energy can be saved when the separation by smelting is combined with scrap preheating.
The extraction method of copper by nonferrous metal baths (2) is based on the fact that the copper solubility in a metal bath of lead [10] or aluminium [11, 12] is higher than that of steel. But for the reduction of the copper content in 1 t of scrap from 0.3 % to 0.1 %, 1000 kg lead would be necessary [10]. In spite of a considerable degree of copper removal, the high lead consumption makes this method unacceptable. The solubility of copper in an aluminium bath is 65 % at 730 °C. At a temperature of 750 °C, 80 % of the copper can be removed in only 20 min [11, 12]. But in this study [11, 12], it is not clear which amount of aluminium-copper-alloy is enclosed in the scrap in a real process.

To remove copper from steel, an extraction method using sulphur-containing slag melts (3) can be used [8] where the slag consists of sodium sulphide and iron sulphide. Copper is concentrated in this slag during the treatment. The sodium sulphide content, e.g., was increased from 19 to 25 % in the temperature range from 800 to 1000 °C [8]. For the treatment of 1 t of scrap, at least 4 kg of slag were necessary to decrease the copper content from 0.3 to 0.1 % under a nitrogen or argon gas atmosphere.

A gas mix of chlorine, hydrogen and air (4) was used for the removal of copper in reference [13]. In this procedure, the surface of the steel parts in the scrap was oxidized by air with respect to the iron loss by chlorination. 74 % of the copper was removed from 3.5 kg of scrap at a time of 90 min. A gas mix consisting of chlorine and air was also used for copper removal [14]. The advantage of this treatment is due to the fact that simultaneously with the copper other tramp elements such as lead and tin can be removed while disadvantages such as:

- the presence of toxic treatment gases
- oxidation of iron,
3.3 Slag extraction

Figure 11 illustrates the conditions of copper removal from steel melts using sulphur-containing slags. The principle is based on the fact that copper sulphide is more stable than iron sulphide at temperatures above 600 °C [8, 10, 15-18].

In various publications, the copper removal capacity of slags based on iron sulphide and sodium sulphide was investigated [10, 15-18]. Together with the slag composition, temperature and composition of the steel bath, especially its carbon content, are important parameters in this removal process. Sodium sulphide, sodium sulphate or sodium carbonate were added to the slag for fluidisation. Because of the rather low copper distribution coefficient, the consumption of S-containing slag is high. For example, a treatment of 1 t of steel requires 100 kg of slag. Another disadvantage of this method is related to increasing sulphur contents in the steel.

\[
2[Cu]+FeS \leftrightarrow Cu_2S+[Fe]
\]

Partition of Cu between slag and steel melt:

\[
L_{Cu} = \frac{\% (Cu)_{slag}}{\% (Cu)_{steel}}
\]

<table>
<thead>
<tr>
<th>Na$_2$S-FeS, Na$_2$SO$_4$-FeS, Na$_2$S-(Al_2O_3) slags (K$_2$SO$_4$, MgSO$_4$ and CaSO$_4$ additions tested)</th>
</tr>
</thead>
</table>

L$_{Cu}$ is increased by

- High Cu activity in the steel melt
- High FeS activity in the slag melt
- Low CuS activity in the slag melt
- Low Fe activity in the steel melt
- Lower temperature

L$_{Cu}$ < 20 at 1300°C for Fe-\(\text{C}_{\text{sat}}\)-Cu melt

Figure 11. Copper removal from steel melts using S-containing slags.
3.4 Other scrap purification methods

Figure 12 shows other methods for copper removal from steel.

The dilution by addition of copper-free material to the steel bath represents an “apparent” purification method but is not acceptable as a “real” long-term metallurgical solution to the problem.

The harmful effect of copper can be balanced out by addition of alloying elements such as Ni and Al\textsuperscript{19}. The addition of nickel in a proportion of 2:1 or 1:1 neutralizes the harmful properties of the copper. In a recent study from Leeds University, England, the increasing of aluminium content in the steel with respect to neutralisation of copper has been investigated\textsuperscript{19}.

An unusual method for copper removal from steel melts has been tested in the Ukraine\textsuperscript{20, 21}. The steel was filtrated using filters from Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} ceramics. The rate of removal was about 30 %. The effect was explained by the absorption of copper on the ceramic surfaces. The injection of ceramic particles into a Cu-containing steel bath caused an increase of the removal rate.

The negative effect of copper on crack formation in construction steels can also be reduced through controlled process management. A decreased secondary cooling rate in continuous casting of copper-containing steels lead to a decrease of crack depth\textsuperscript{22} (Figure 12).

\begin{quote}
(1) Dilution by addition of copper-free material (hot metal, sponge iron). \textit{No long-term metallurgical solution to the problem}

(2) Balancing-out of harmful Cu effects by addition of alloying elements (Ni, Al). Ref.\textsuperscript{19}

(3) Filtration of steel melts through ceramic filters\textsuperscript{20, 21}.
  - \textit{Absorption of copper on ceramic surfaces}
  - \textit{Absorption of copper on ceramic particles (Al\textsubscript{2}O\textsubscript{3}, ZrO-C, e.g.) injected into the steel bath}

(4) Reduction of negative effects through controlled process management (e.g. decreased secondary cooling rate in continuous casting)\textsuperscript{22}
\end{quote}

\textbf{Figure 12.} Further methods of copper removal from steel\textsuperscript{19-22}. 

\textit{RMZ-M\&G 2003, 50}
3.5 Vacuum distillation

Copper can be removed from steel baths by vacuum distillation. This separation method is based on the distinct differences in vapour pressure between copper and steel. The copper vaporizes both in the elementary state [23] and in the form of volatile copper compounds [24, 25].

The vacuum distillation of copper and tin-containing steel melts has been investigated in a vacuum induction furnace [23] (Figure 13). It was found that the removal of a considerable amount of copper and tin from steel melts under reduced pressure is possible (Figure 13). The reduced pressure was the main factor in the vacuum distillation process, which must be below 1 mbar. The decrease of the gas pressure in the range from 1 to 0.1 mbar leads to a clear increase of the distillation rate of copper, while a further decrease of the gas pressure below 0.1 mbar does not influence the distillation rate. In this range of pressure the distillation rate is determined by diffusion in the steel melt rather than by gas diffusion or free surface vaporization.

The ratio of free-surface to volume of the steel melt also has a considerable influence on the distillation rate. The steel bath surface during vacuum distillation must be free from slag and reaction products in order to avoid blockage of the distillation.

The distillation rate further increases with increasing steel bath temperature (Figure 13), and intensified stirring. Inductive stirring of the steel bath, e.g., in the vacuum induction furnace, generates a strong flow field, which is unfavourable for vacuum distillation from the free surface. Turbulence of the steel flow near the free surface becomes as a main influencing factor on the distillation rate when diffusion in the steel bath is negligible.

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Separation method making use of distinct differences in vapour pressure

Vapour pressures of pure metals at 1600°C (mbar):

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pressure (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>69750</td>
</tr>
<tr>
<td>Mn</td>
<td>53</td>
</tr>
<tr>
<td>Sn</td>
<td>1.32</td>
</tr>
<tr>
<td>Cu</td>
<td>1.26</td>
</tr>
<tr>
<td>Fe</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Vacuum melting unit (Ref. [23]): vacuum induction furnace max. 100kW, 3kHZ, 20kg of steel, crucible diameter 15cm, depth of bath 16cm, argon gas.

Parameters of vacuum treatment:

gas pressure (0.01-1.0 mbar)
temperature (1400-1600°C)
chemical composition of steel melt
stirring intensity

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Figure 13. Copper removal from steel melts by vacuum distillation [23].
4 SUMMARY AND OUTLOOK

In the present paper the methods of removal of tramp elements such as copper and tin from steel scrap are presented. Theoretical concepts and methods of steel scrap purification have been discussed along with details regarding practical performance.

5 REFERENCES


Baker in kositer v recikliranem starem železu