上海大学出版社

2005年上海大学博士学位论文 20

金属循环过程中渣化法分离铁与铜锡等元素技术的基础研究

● 作者：李长荣

● 专业：钢铁冶金

● 导师：蒋国昌　洪　新

2005年上海大学博士学位论文 20

金属循环过程中渣化法分离铁与铜锡等元素技术的基础研究

作　　者：李长荣
专　　业：钢铁冶金
导　　师：蒋国昌　洪　新

上海大学出版社
·上海·

Shanghai University Doctoral
Dissertation (2005)

Foundational Study on Separating Technique of Copper, Tin and Other Elements from Iron by Slagging Method in Metal Recycling

Candidate: Li Changrong
Major: ferrous metallurgy
Supervisor: Prof. Jiang Guochang Prof. Hong Xin

Shanghai University Press
· Shanghai ·

上 海 大 学

本论文经答辩委员会全体委员审查，确认符合上海大学博士学位论文质量要求.

答辩委员会名单：

主任：	李大经	教授，上海应用技术学院	200235
委员：	周渝生	教授级高工，上海宝钢集团	201900
	齐渊洪	教授级高工，北京钢铁研究总院	100081
	毛协民	教授，上海大学	200072
	徐建伦	教授，上海大学	200072
导师：	蒋国昌	教授，上海大学	200072
	洪　新	教授，上海大学	200072

评阅人名单：

蒋升喜	教授级高工，北京矿冶研究总院	100044
齐渊洪	教授级高工，北京钢铁研究总院	100081
姜周华	教授，东北大学	110004

评议人名单：

吴　铿	教授，北京科技大学	100083
谢蕴国	教授，昆明理工大学	650093
方　园	教授级高工，上海宝钢集团	201900
石洪志	教授级高工，上海宝钢集团	201900
吴晓春	教授，上海大学	200072
徐建伦	教授，上海大学	200072

答辩委员会对论文的评语

博士研究生李长荣提交的学位论文中详尽地评述了国内外在废钢残存元素分离方面已经开展的研究工作，把握该领域的研究动态和发展趋势，所提出的渣化法分离铁与铜锡等元素技术的研究课题具有重大的学术价值和良好的应用前景，对研究更为有效的金属循环利用技术具有开创性的意义．该论文研究主要有以下几个方面的创新和成果：

(1) 在实验室条件下，首次针对渣化法的熔渣体系研究了铜、锡在高 FeO 熔渣中的氧化溶解特性，验证了它们在熔渣中的存在形式，计算了它们的活度系数等数据并获得了有工艺参考价值的研究结论；

(2) 在高温条件下研究了铜、锡元素在富 FeO 熔渣与金属溶液之间的分配规律．指出了渣化法分离铁与铜、锡等元素技术的熔渣体系选择的基本原则；并在实验室条件下成功地实现了铁与铜、锡、砷、锑、铋等元素 87%以上的高分离效率，有效地将多种有价元素同时富集于钢水残液中；

(3) 对实验中获得的熔渣进行的显微观察和微区成分分析对熔渣的后续处理具有重要工艺参考价值．

全文立论正确、内容充实、结构严谨、文笔流畅、论文撰写规范，文中所涉及的实验方法和测试技术可行、得出的数据翔实可信、结论合理正确．论文答辩过程中，论点清晰、叙述清楚、逻辑性强，回答问题正确．综上所述，可以看出作者具有扎实的基础理论知识、良好的科研素养和较强的科研创

新能力，他的论文和答辩已达到博士学位要求.

答辩委员会由5人组成，经投票表决，以全票通过李长荣的博士学位论文答辩，建议授予其博士学位，并推荐为优秀博士论文.

答辩委员会表决结果

经答辩委员会表决，全票同意通过李长荣同学的博士学位论文答辩，建议授予工学博士学位.

答辩委员会主席：**李大经**

2004年11月30日

摘　要

尽管不断有各种各样的新材料问世，工程材料也日趋多元化，但钢铁材料仍是现代人类社会最广泛使用的材料. 在目前使用的金属材料当中，钢铁所占的比例在 90% 以上. 随着地球矿产资源的迅速枯竭，废钢必将成为钢铁生产的主要原料来源. 因此，逐步建立以废钢铁为原料基础的钢铁冶金体系，是社会可持续发展的重要组成部分，是建立循环型经济社会的必然要求.

本文论述了废钢循环在整个循环经济活动中的重要性及其在钢铁材料可持续发展中的关键作用，首次明确地指出了采用稀释法利用回收废钢方法的负面效应，这种利用方式还是停留在线性经济的思维定式里. 此类仅以成本最低为原则的利用模式已经不符合循环经济的发展要求.

理论研究和生产实践都表明：钢材的纯净度对其性能和使用寿命都具有很大的影响. 在金属循环过程中维护和保持金属基体的纯净性是至关重要的，未来废钢价值的大小将主要取决于废钢中有害残存元素的含量.

本文对渣化法分离黑色金属与有色金属元素技术的基本原理进行了论述和分析. 对废钢中最为常见的有害残存元素铜、锡在富 FeO 熔渣中的氧化溶解行为进行了研究. 在 1 873 K

温度条件下，与金属铜溶液平衡的纯氧化铁熔渣中含铜量为2.04%，熔渣中的铜含量随着渣中CaO含量的增加而逐渐减小.根据实验结果计算出$\gamma CuO_{0.5}$，并得出$\gamma CuO_{0.5}$与熔渣中CaO含量之间的关系：

$$\gamma CuO_{0.5}=3.95-2.31\exp(-(CaO\%)/16.63).$$

在1 873 K温度条件下，与金属锡溶液平衡的纯氧化铁熔渣中含锡量为8.07%.锡的氧化溶解随着熔渣中CaO含量的增加仅略有下降，说明CaO含量对锡的氧化溶解的影响小于其对铜氧化溶解的影响.相比之下，锡的氧化溶解更容易受到氧分压的影响.得出的γSnO与熔渣中CaO含量之间的关系为：

$$\gamma SnO=1.37-0.021(CaO\%).$$

采用化学平衡法对铜、锡元素在富FeO熔渣与金属液之间的分配规律进行了研究.研究结果表明：在1 823～1 923 K的温度范围内，得出的(Cu%)与温度之间的关系为：

$$当[Cu]=10\%时，(Cu\%)=-1.18+8-10^{-4}T;$$

$$当[Cu]=1.96\%时，(Cu\%)=-0.75+5\times10^{-4}T.$$

而在[Sn]=0.71%时，温度对锡在渣金间分配的影响甚微.铜在渣金间的分配比随着温度的升高而升高，但温度对低浓度下的分配比影响更大一些，在高浓度时其影响变小，分配比的增势明显变缓.

根据渣金间的化学平衡研究了铜在富FeO熔渣与金属溶

液之间的分配比，当[Cu]<20%时，得出了熔渣中($CuO_{0.5}$%)与[Cu%]之间的关系为：

$$(CuO_{0.5}\%) = \{0.069\,22\exp(-0.105\,5[Cu\%]) + 0.021\,6\}[Cu\%].$$

对于[Cu]>20%时，用下式表示则更为简单：

$$(Cu\%) = 0.019\,24[Cu\%] + 0.118\,04.$$

L_{Cu}与铜浓度之间的关系为：

$$L_{Cu} = 0.09\exp(-[Cu]/2.302\,41) + 0.112\,8\exp(-[Cu]/43.300) + 0.018\,88.$$

富 FeO 熔渣的成分对铜在渣金间的分配比有重要影响，适量的 CaO 有利于降低铜在熔渣中的溶解.在 Fe-Cu 溶液中同样铜含量的情况下，随着熔渣中氧化钙含量的增加，熔渣中 Cu 含量降低.CaO 的影响在 Fe-Cu 溶液中铜含量较低时相对较小，随着溶液中铜含量的升高，其影响逐渐变大，在纯铜溶液时为最大.在本研究条件下，熔渣中 SiO_2 含量的增加，会使熔渣中铜的氧化溶解增大.

在实验室感应炉冶炼的条件下，对废钢溶液进行了渣化实验研究.研究表明：感应炉内的渣金反应没有达到平衡，实测值与计算的平衡值有一定差距.吹氧方式的不同对熔渣中的铜、锡含量是有影响的，同样的 Cu 含量条件下，深吹氧方式获得的富 FeO 熔渣中铜含量约比表面吹氧方式获得的熔渣高约 30%.

渣化实验实现了多种有色金属 Cu、Sn、As、Sb、Bi 等元素在

废钢溶液中的同时富集，并获得了可以满足炼铁生产要求的富FeO熔渣．铁、铜的元素分离效率为87%，铁、锡的元素分离效率达到94%，其他元素的分离效率也在90%以上．

关键词 废钢循环，残余元素，渣化法，富FeO熔渣，元素分离，金属残液

Abstract

Iron and steel is still the most widely used material in modern human-being society, although various engineering materials have been continuously developing and become diversified day by day. Up to date steel products account for more than 90% in all metal materials that have been consumed. With the rapid depletion of the ore resource in the earth, scrap must become the main source of raw materials in steel making. With this reason it is necessary to establish step by step the iron and steel production system based on scrap. This is also an inevitable requirement and an important and indispensable part of foundations for a sustainable society.

The importance of scrap steel recycling in whole circular economy and its key role in iron and steel production were discussed and reviewed in this dissertation. The author definitely pointed out unprecedented the negative respect of present way to recycle scrap with dilution method, which belong to still the linear economy ideas. This kind of style based on the only principle of lowest-cost can never meet the requirement of circular economy.

It was approved both by the theory and by practice that the quality of steel and its service life were greatly affected by the purity of steel. Steel production would have qualitative

change when the content of impurity in steel reduced to certain level. To maintain and keep the purity of matrix materials is critical important in the metal recycling. The value of scrap steel will be mainly decided by the content of harmful residual elements within scrap in the near future.

The basic principle of the slagging method to separate ferrous and non-ferrous elements technology was discussed and analyzed. The dissolve behavior of copper and tin in FeO-rich slag was investigated. The copper content in the pure FeO slag was 2.04% as the slag was equilibrium with metal copper under the temperature of 1 873 K. The copper content in slag went down gradually with the increase of CaO content in the slag. Activity coefficient $\gamma CuO_{0.5}$ was calculated based on the results of experiments. The relationship between $\gamma CuO_{0.5}$ and CaO content in slag was deduced by fitting the experimental curve:

$$\gamma CuO_{0.5} = 3.95 - 2.31\exp(-(CaO\%)/16.63).$$

The tin content in the pure FeO slag reached 8.07% as the slag is equilibrium with metal tin under the temperature of 1 873 K. The tin content in slag went down slightly with the increase of CaO content. The dissolve of tin in slag tended to be more affectively by oxygen partial pressure. The relationship between γSnO and CaO content in slag was deduced by fitting the experimental curve:

$$\gamma SnO = 1.37 - 0.021(CaO\%).$$

The distribution behavior of copper and tin between

FeO-rich slag and metal were studied with the chemical equilibrium method. The results indicated that within the temperature range of 1 823～1 923 K, the relationship between temperature and (Cu%) was expressed as follows:

$$(Cu\%) = -1.18 + 8 \times 10^{-4} T, \text{ while } [Cu] = 10\%;$$

$$(Cu\%) = -0.75 + 5 \times 10^{-4} T, \text{ while } [Cu] = 1.96\%.$$

The influence of temperature to the distribution of tin between the slag and metal was quite slight while [Sn] = 0.71%. The distribution ratio of copper between slag and metal went up with the raise of temperature. But its influence to the distribution ratio at low copper concentrate was more obvious than at higher copper concentrate. And the increment of increase became plainness as [Cu] content was higher.

The distribution ratio of copper between FeO-rich slag and metal was investigated in terms of chemical equilibrium. The relationship between ($CuO_{0.5}$%) and [Cu%], as [Cu%] is less than 20%, showed:

$$(CuO_{0.5}\%) = \{0.069\,22\exp(-0.105\,5[Cu\%]) + 0.021\,6\}[Cu\%].$$

And as [Cu%] is more than 20%, the expression as follow is more simplification:

$$(Cu\%) = 0.019\,24[Cu\%] + 0.118\,04.$$

The relationship of L_{Cu} and [Cu] content was:

$$L_{Cu} = 0.09\exp(-[Cu]/2.302\,41) +$$

$$0.1128\exp(-[Cu]/43.300)+0.01888.$$

The composition of the FeO-rich slag influences greatly on the distribution ratio of copper between slag and metal. And proper CaO content in slag may reduce the dissolve of copper in the slag. With the increase of CaO content in slag, the copper content in slag will decrease when the copper content in metal is the same. The influence of CaO content was relatively smaller while [Cu] content was lower and it became greater with the [Cu] content increasing, it reached the maximum as the solution was metal copper. The increment of SiO_2 content in the slag made the copper dissolve to be larger under the given experiment conditions.

Under the condition of an induction furnace, the slagging experiments of scrap steel molten were carried out. The results showed that the difference of oxygen blowing had some influence on copper and tin content in the slag. The copper content in the FeO-rich slag gained by the measure of the under-surface oxygen blowing is 30% more than that gained by the top-surface oxygen blowing at the same [Cu] content.

The investigations showed that the reactions between slag and metal did not reach the equilibrium status. There was difference between the measured value and the calculated equilibrium value. The distribution ratio of copper between slag and metal was able to be reduced by properly adding CaO into slag.

The simultaneous enrichment of various elements, such

as Cu, Sn, As, Sb, Bi , in the metal residual liquid was carried out by slagging the scrap steel molten, which FeO-rich slag could be satisfy the requirement of ironmaking process. The separating efficiency of iron and copper element was 87%, the separating efficiency of iron and tin element was 94%, and separating efficiency of other elements was also over than 90%.

Key words scrap recycle, residual elements, slagging method, FeO-rich slag, elements separate technology, metal residual liquid

目　　录