

Phase Equilibrium between Ni-S or Ni-Fe Melt and Slag in Nickel Smelting (ニッケル溶錬系におけるNi-SまたはNi-Fe融体とスラグ間の相平衡)

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学位論文題目 Phase Equilibrium between Ni-S or Ni-Fe Melt and Slag
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スラグ間の相平衡)

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論文内容要旨

1. Introduction

As a contribution to understand the nickel smelting process and investigate new options for nickel smelting production, the present study has been conducted to thermodynamically evaluate the direct conversion of nickel sulfide to metallic nickel as well as the reduction of oxide ores containing nickel and iron to ferro-nickel alloys. The phase equilibrium and distribution of some minor elements between nickel based alloys and slags have been systematically investigated mostly in a MgO crucible at 1773 and 1873 K. A predominant objective in the present study was to investigate and look for the slag or the flux suitable for direct converting of Ni_3S_2 to metallic nickel. Thus, the Ni-S alloy was equilibrated with the $\text{FeO}_x\text{-SiO}_2\text{-MgO}$, $\text{FeO}_x\text{-CaO-MgO}$ or $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ slag under controlled partial pressures of S_2 and O_2 . The partial pressure of SO_2 was controlled at 0.1 MPa by assuming that the Ni-S melt is oxidized by blowing air. Another part of this work was devoted to the fundamental study of ferro-nickel smelting. For this objective, the Fe-Ni based alloy was equilibrated with the $\text{FeO}_x\text{-SiO}_2\text{-MgO}$, $\text{FeO}_x\text{-CaO-SiO}_2\text{-MgO}$ or $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ slag to obtain the information of metal loss into the slag and behavior of some minor elements.

2. Ni-S Melt / Slag Equilibration

The $\text{FeO}_x\text{-CaO-MgO}$, $\text{FeO}_x\text{-SiO}_2\text{-MgO}$ or $\text{CaO-Al}_2\text{O}_3$ melt in the MgO crucible was found to form a homogeneous liquid. On the contrary, the $\text{CaO-Al}_2\text{O}_3$ melt in the Al_2O_3 crucible coexisted with a solid solution of $\text{Al}_2\text{O}_3\text{-NiO}$.

The obtained relationship between the content of nickel in the slag and that of sulfur in the alloy, as shown in Figure 1, is helpful to summarize the experimental results. It is noted that the solubility of nickel in the slag increases when the content of sulfur in the alloy decreases. It was found that, for a given content of sulfur in the alloy, CaO-Al₂O₃-MgO and FeO_x-CaO-MgO slags represent lower and higher solubility of nickel, respectively. Figure 1 also indicates that the nickel solubility in the CaO-Al₂O₃-MgO slag decreases by increasing temperature. The compositions of slags and alloys near the anticipated precipitation of solid NiO are shown in Table 1. The contents of iron remaining in the alloy for the equilibrium with the FeO_x-CaO-MgO or FeO_x-SiO₂-MgO slag are around 1 and 2%, respectively. In this condition, the content of nickel in the slag is higher than 10%. Elimination of sulfur and oxygen from the nickel alloy will be required. However, the present results indicate that, by equilibrating the Ni-S melt with the CaO-Al₂O₃-MgO slag at 1873 K, the contents of sulfur and oxygen are reduced considerably with appreciable reduction in the solubility of nickel in the slag.

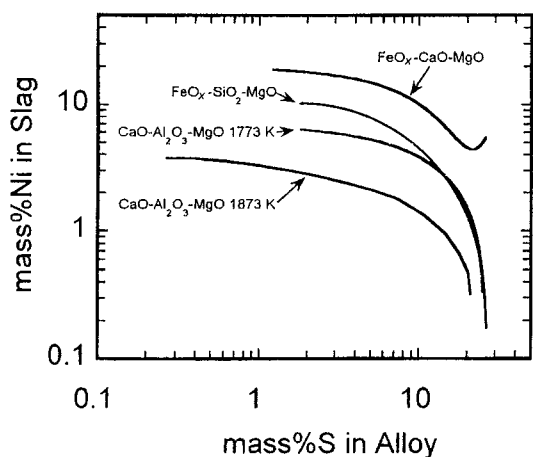


Figure 1 Relationship between content of nickel in slag and content of sulfur in alloy for Ni-S melt equilibrated with slags

Table 1 Compositions of melt and slag at p_{O_2} just before precipitation of NiO

Slag System	Nickel (mass%)			Slag (mass%)
	S	Fe	O	Ni
FeO _x -CaO-MgO 1773 K	2	1	0.5	20
FeO _x -SiO ₂ -MgO 1773 K	2	2	0.5	10
Al ₂ O ₃ -CaO-MgO 1773 K	1	—	0.4	6
Al ₂ O ₃ -CaO-MgO 1873 K	0.4	—	0.2	4

The behavior of some minor elements in the CaO-Al₂O₃-MgO slag at 1873 K has been investigated to understand the elimination of impurities or the loss of valuable metals. It was suggested from the experimental results that phosphorus and iron preferentially dissolve in the slag phase while nickel, copper, silver, platinum, gold, arsenic and antimony mostly remain in the alloy phase. Cobalt is distributed in both phases.

The behavior of nickel and minor elements was discussed thermodynamically by combining the oxidic and sulfidic dissolution of the species in the slag. The present results indicate that Ni dissolves as NiO in the

slag except for the $\text{FeO}_x\text{-CaO-MgO}$ slag, in which nickel is dissolved as $\text{NiS}_{0.66}$ and NiO in the ranges of lower p_{O_2} and higher p_{O_2} , respectively. For the minor elements, the predominant species of copper, cobalt and silver in the $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ slag at 1873 K are $\text{CuO}_{0.5}$, CoO and $\text{AgO}_{0.5}$, respectively. Sulfidic dissolution prevails in all the range of p_{O_2} for arsenic and gold while oxidic dissolution predominates at higher p_{O_2} for antimony.

3. Ni-Fe Melt/ Slag Equilibration

The phase relation between the Ni-Fe alloy and the $\text{FeO}_x\text{-MgO-SiO}_2$, $\text{FeO}_x\text{-MgO-SiO}_2\text{-CaO}$ or $\text{FeO}_x\text{-MgO-SiO}_2\text{-AlO}_{1.5}$ slag and the distribution of nickel, chromium, manganese, cobalt and copper between these phases in a magnesia crucible were investigated at 1773 and 1873 K. It was suggested from the experimental results that chromium and manganese preferentially dissolve into the slag phase while nickel, cobalt and copper mostly remain in the alloy phase. Increase in the temperature reduces the dissolution of chromium into the slag. The addition of lime in the plain slag reduces the dissolution of chromium and manganese into the slag. The addition of alumina reduces the dissolution of nickel, cobalt and copper while increases that of chromium. It was indicated that the predominant species of nickel, chromium, manganese, cobalt and copper in the slags are NiO , $\text{CrO}_{1.5}$, MnO , CoO and $\text{CuO}_{0.5}$, respectively.

4. Applications for Nickel Production from Ni-S or Ni-Fe-S Melt

The nickel contents in the alloys equilibrated with the $\text{FeO}_x\text{-SiO}_2$ and $\text{FeO}_x\text{-CaO}$ slags (fluxes) in a MgO crucible at 1773 K and p_{O_2} just before precipitation of solid NiO are relatively large at more than 95 mass%, but the amounts of iron, sulfur and oxygen are considerable. Thus, when a process of smelting the Ni-S or Ni-Fe-S alloy with the $\text{FeO}_x\text{-SiO}_2$ and $\text{FeO}_x\text{-CaO}$ based slags (fluxes) is considered, a refining process for the metal product will be indispensable. Furthermore, it is noted that the content of nickel in the iron slag is considerably large at more than 10 mass%. This means that the loss of nickel in the slag will be substantial in the smelting process. A simple mass balance calculation by assuming smelting of a matte with 50 mass% of nickel and 25 mass% of iron to produce a metal phase with 2 mass% of iron and 2.5 mass% of sulfur and a slag phase with 40 mass% of iron indicated that the loss of nickel in the $\text{FeO}_x\text{-SiO}_2$ and $\text{FeO}_x\text{-CaO}$ based slags amount to 12 and 24 mass%, respectively. The loss of nickel would increase with increasing content of iron in the initial matte phase or with reducing content of iron in the initial slag phase.

The present study clarified that the content of nickel in the slag is not so high in the iron-free fluxes such as $\text{Al}_2\text{O}_3\text{-CaO-MgO}$ system. Furthermore, the amount of produced slag in the process would be kept small to reduce the loss of nickel in the slag. Thus, it was suggested that the $\text{CaO-Al}_2\text{O}_3$ based slag will be more useful for converting the Ni-S melt to liquid nickel.

It was found in the present study that the solid solution was precipitated in the $\text{CaO-Al}_2\text{O}_3$ based slag melted in the Al_2O_3 crucible at 1773 K. The use of this heterogeneous slag for the nickel smelting at 1773 K may cause a build-up problem with the accretion in the furnace or result in the enhancement of slag viscosity, both will make the smelting operation seriously difficult. Hence, the use of Al_2O_3 based refractory has to be avoided. The amounts of impurities such as sulfur and oxygen contained in the alloys equilibrated with the

CaO-Al₂O₃-MgO slag can be reduced substantially by increasing the temperature from 1773 to 1873 K. Minor elements such as phosphorous, iron and cobalt would be removed in more or less extent in the slag phase. However, it will be very difficult to remove arsenic and antimony in the Ni-S melt into the slag. Gold, silver and platinum will remain mostly in the Ni-S melt.

The present work clarified that the CaO-Al₂O₃ based slag melted in the MgO crucible at 1873 K would be suitable for direct converting of Ni₃S₂ to metallic nickel. This slag makes a homogeneous liquid phase and represents lower solubility of nickel and higher solubility of some detrimental minor elements. In addition, the metallic nickel has less contents of sulfur and oxygen. However, for further reduction of impurities in the metal, a refining process for the metal product will be indispensable.

5. Applications for Fe-Ni Production

The addition of CaO into the slag depressed the solubility of nickel in the slag and the effect is more pronounced by the addition of Al₂O₃. However, as the total loss of nickel in the slag is a function of the slag quantity, smelting the ores containing CaO or Al₂O₃ will produce a larger tonnage of slag, that results in the increase of nickel loss. Thus, the optimum slag composition should be considered for the economical evaluation.

Chromium, copper, cobalt and manganese are considered as undesirable impurities in the ferronickel production. Operating the ferronickel process at higher temperature makes the elimination of chromium more difficult. The addition of lime will not favor the removal of chromium and manganese from the Ni-Fe alloy. On the other hand, the removal of chromium is better affected by the addition of alumina into the slag while the removal of cobalt and copper would be decreased.

論文審査結果の要旨

ニッケルの乾式製錬プロセスの高効率化と製品の品質管理を図るうえで、ニッケルの溶解損失量が少なく、不純物の除去効果の大きいスラグ・フラックスの選択が重要である。本研究は、Ni-S 系融体ないしは熔融 Ni-Fe 合金と $\text{FeO}_x\text{-SiO}_2$ 基、 $\text{FeO}_x\text{-CaO}$ 基、 $\text{Al}_2\text{O}_3\text{-CaO}$ 基などの各種スラグ間の相平衡関係および成分の分配挙動を体系的に調べたもので、全編7章からなる。

第1章は緒論であり、本研究の意義と目的について述べている。

第2章では、空気による硫化鉍溶錬に相当する亜硫酸ガス分圧が 0.01 MPa の条件下における Ni-S 系融体とスラグ間の相平衡実験方法を検討し、 Ni_3S_2 から NiO に至る広いポテンシャル域において酸素および硫黄の分圧を精度良く制御できる $\text{CO}\cdot\text{CO}_2\cdot\text{SO}_2$ 混合ガス法の確立に成功している。

第3章では、マグネシアるつぼ中における Ni-S 系融体と $\text{FeO}_x\text{-SiO}_2$ 基ないしは $\text{FeO}_x\text{-CaO}$ 基スラグ間の相平衡実験を 1773K で行い、NiO の出現する 10 Pa 程度の高酸素分圧下において、スラグ中のニッケルおよび金属ニッケル中の鉄、硫黄、酸素濃度が、それぞれ、10 mass% および 1~2、2、0.5 mass% に達するので、スラグ中のニッケルの回収と金属ニッケルの精製が必要となることを明らかにしている。

第4章では、マグネシアおよびアルミナるつぼ中における Ni-S 系融体と $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{MgO}$ 基スラグ間の相平衡を 1773K で調べ、マグネシアるつぼ中での溶解平衡の場合、NiO が出現する高酸素分圧下においてもスラグ中のニッケル溶解量が 6 mass% 程度のかかなり小さな値を呈するが、アルミナるつぼ中での溶解の場合、スラグ融体中にスピネル固相が析出するので円滑な製錬操作が妨げられる恐れがあることを提示している。

第5章では、マグネシアるつぼ中における Ni-S 系融体と $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{MgO}$ 基スラグ間の相平衡および不純物の分配をより高温度の 1873K で調べ、スラグ中へのニッケル溶解量および金属ニッケル中の硫黄含有量が、それぞれ、4 および 0.4 mass% まで低減するので、ニッケルのスラグ溶解の抑制と低硫黄含有金属ニッケルの生成に溶錬温度の上昇が効果的であること、ヒ素、アンチモン、金、銀などの微量成分が金属ニッケル相中に濃縮されるので、これらの除去・回収が必要とされること、などを明らかにしている。

第6章では、熔融 Ni-Fe 合金と $\text{FeO}_x\text{-SiO}_2\cdot\text{MgO}$ 基スラグ間の成分元素および不純物の分配に及ぼす Al_2O_3 および CaO の影響について調べ、スラグへの Al_2O_3 および CaO の添加が、それぞれ、ニッケル、コバルト、銅およびクロム、マンガンのスラグ溶解を抑制することを見出している。

第7章は、本研究の全体から得られた結果の総括である。

以上要するに本論文は、熔融 Ni-S および Ni-Fe 合金と各種スラグ間の相平衡における成分元素および不純物の挙動を体系的に解明し、ニッケル硫化鉍および酸化鉍の溶錬に適したスラグ・フラックスについて考究したもので、金属工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。