Introduction

Metals that are rare or considerably difficult to be extracted from natural resources economically or physically are referred to as rare metals. Rare metals have become essential resources for the Japanese industry because they are used for manufacturing iron and steel materials, including stainless steel, automobiles, and high-technology products such as electrical and electronic equipments. However, Japan depends on foreign countries for most of its requirements of rare metals. A stable supply of rare metal resources is the most important issue for further development of the Japanese industry. With regard to this issue, Japan maintains stockpiles of seven kinds of rare metals (Ni, Cr, W, Co, Mo, Mn, and V).1)

Information concerning the supply, demand, and flow of rare metals is necessary to deliberate on the material cycle and resources strategy. However, the national statistics on the availability of these resources, which are described in brief in the Yearbook of Iron and Steel, Non-Ferrous Metals, and the Fabricated Metals Statistics of the Ministry of Economy, Trade and Industry (METI),2) are inadequate. In order to complement this inadequacy in information, the Japan Oil, Gas and Metals National Corporation (JOGMEC), Japan Rare Metal Association (RMA), and research institutes have actively conducted material flow analysis (MFA) and substance flow analysis (SFA).3–5) The MFA/SFA methods, which are employed for studying and controlling material flow, are paid attention worldwide. In foreign countries, Brunner reviewed the history and prospects of using MFA,6) Gradel et al. proposed a new method of MFA,7,8) and the Wuppertal Institute for Climate, Environment and Energy estimated the flow of resources involved in the use of materials.9) In Japan, the authors have developed the MFA/SFA methods based on the waste input-output (WIO)10,11) table, and they have collected and assessed data on the material/substance flow.12–14) This study focuses on manganese (Mn), which is one of the seven rare metals stockpiled by the National Stockpile Program; the data on Mn flow is collected and assessed.

Figure 1 shows the demand for Mn in Japan in 2004. This is drawn based on the data compiled by JOGMEC.3) Manganese is used as an additive in the manufacturing of iron and steel in order to develop hardness, wear resistance, and corrosion resistance; further it is also used as a deoxidizing and desulfurizing agent due to its strong affinity for oxygen and sulfur. It is an indispensable material in the steel industry. Moreover, it is also used as a raw material for Mn dry cells, aluminum alloys, and ferrite magnets. Approximately 95% of the global demand for Mn is for iron and steel manufacturing.15)

The flow of Mn in the steel industry is mainly in the form of (1) additives in the steelmaking process, which accounts for 95% of the demand for Mn, along with the data collection and assessment of material/substance flow; as a result, an efficient material cycle system is formulated for the Mn flow. The main conclusions are (1) Mn charged as iron ore and the Mn content of other ferrous raw materials reached 266.2×10^3 t-Mn of which 208.9×10^3 t-Mn was discharged as pig iron and 55.4×10^3 t-Mn as blast furnace slag in the ironmaking process, and (2) 530.7×10^3 t-Mn was discharged as steelmaking slag and 577.6×10^3 t-Mn was charged in the secondary refining process as Ferro-Mn, Si-Mn, and metal Mn for the purpose of adding them as constituents of alloy in the steelmaking process.

KEY WORDS: substance flow analysis; material flow analysis; manganese; iron; steel; slag; recycle.
clude deoxidizers and constituents of alloyed steel, and (2) iron ore and iron scrap. The former form of Mn is actively employed in the secondary refining process of steelmaking, and its consumption pattern can be obtained from the data compiled by JOGMEC\(^ \text{16)} \) and the statistics compiled by METI\(^ \text{17)} \). On the other hand, the latter form of Mn is transferred into steelmaking slag and blast furnace slag. The MFA/SFA of Mn, including the latter case, has not been conducted in Japan. The present study conducts the SFA of Mn with regard to the iron and steel cycle, which accounts for 95% of the demand for Mn, along with the data collection and assessment of material/substance flow; as a result, an efficient material cycle system is formulated for the Mn flow.

2. Review of the Mn Flow in Japan

The Mn flow in Japan can be studied from the data compiled by JOGMEC\(^ \text{3,15,16)} \). The data on the supply and demand of Mn can be obtained from the abovementioned data compiled by JOGMEC and RMA\(^ \text{4)} \) and the Industrial Rare Metals Annual Review\(^ \text{18)} \).

**Figure 2** shows the changes in the global supply and demand of Mn-containing ferroalloys and the changes in the volume of crude steel production in Japan and China based on the data compiled by JOGMEC\(^ \text{15)} \) and the International Iron and Steel Institute (IISI).\(^ \text{19)} \) The supply and demand of ferromanganese (Ferro-Mn) is the highest in China. In 2005, the supply and demand of Ferro-Mn in China were 4.449\( \times 10^6 \) t (41.8%) and 3.795\( \times 10^6 \) t (34.2%), respectively. The demand for Ferro-Mn has shown an upward trend in recent years presumably because of the increase in crude steel production in China. Considering the oligopolistic tendency of the Ferro-Mn market and the expansion of crude steel production in China, the surge in international prices, and the tight supply and demand in the world following a production failure in 2004, securing resources, including recycling, will become more important. Although the demand exceeded the supply in 2005 and 2006, the differences were balanced with supplies from the stockpiles.

**Figure 3** shows the Mn flow in Japan in 2005 based on the data compiled by JOGMEC.\(^ \text{16)} \) The sources of Mn in the steelmaking industry are high-carbon ferromanganese (Ferro-Mn (High-C)), low- and medium-carbon ferromanganese (Ferro-Mn (Low/Medium-C)), silicon manganese (Si–Mn), and metal manganese (Metal Mn). The consumption of these materials in terms of pure Mn are obtained from the data compiled by JOGMEC. The consumption of Ferro-Mn and Si–Mn are obtained from the statistics compiled by METI\(^ \text{17)} \) and their values in terms of pure Mn are calculated from the Mn content obtained from the data compiled by JOGMEC\(^ \text{16)} \) as shown in Fig. 3. According to JOGMEC, the consumption of Mn in the steelmaking industry in 2005 was 618\( \times 10^3 \) t-Mn. However, the (a) Mn flow derived from iron ore and (b) Mn flow discharged as slag are not accounted for in the Mn flow chart in Fig. 3.

3. Substance Flow Analysis of Mn Associated with the Iron and Steel Cycle in Japan

3.1. Mn Flow in the Ironmaking Process

The production of pig iron for steelmaking was reported as 8.22\( \times 10^7 \) t in 2005. The amount of blast furnace slag produced as a result of the pig iron production (8.22\( \times 10^7 \) t) was calculated as 2.38\( \times 10^7 \) t. This calculation was based on the amount of blast furnace slag produced during the production of pig iron per ton, as published by the Nippon Slag Association. Because the data in the calendar year 2005 (from January 2005 to December 2005) was not available, the value (0.290 t) in the fiscal year 2005 (from April 2005 to March 2006) was used for the calculation.

**Figure 4** shows the calculation procedure for determining the Mn flow in the ironmaking process. Table 1 shows...
the basis for the calculation. In the ironmaking process, pig iron is produced as the main product and slag is generated as a by-product in the blast furnace (BF).

The weighted average for the Mn content in pig iron, the main product, was estimated as 0.25% by our survey. The MnO content in the blast furnace slag per ton was estimated as 0.3 t-MnO from the data compiled by the Nippon Slag Association. Since the composition of the blast furnace slag does not vary considerably unless the iron ore grades and operating conditions of the sintering process do not change markedly, it may be reasonable to use an average value of MnO content published by the Nippon Slag Association for the calculation of Mn substance flow.

The major sources of Mn in the ironmaking process are iron ore, ferruginous Mn ore, and steel scrap. According to our survey, the weighted average of iron ore consumption for pig iron manufacturing per ton in 2005 was 1.608 t-ore, and that of ferruginous Mn ore consumption was 0.065 × 10^3 t-ore. The consumption of steel scrap for pig iron manufacturing per ton was estimated as 1.495 × 10^3 t on the basis of the statistics compiled by METI and the Japan ferrous raw materials association. The Mn content in the scrap, which was charged into the blast furnace, was assumed to be equivalent to that of pig iron.

Figure 5 shows the Mn flow in the ironmaking process for steelmaking in 2005. The calculations revealed that the Mn input into the blast furnaces as iron ore and other ferrous raw materials reached 266.2 × 10^3 t-Mn of which 208.9 × 10^3 t-Mn was discharged as pig iron and 55.4 × 10^3 t-Mn was distributed into blast furnace slag. The difference of 1.9 × 10^3 t-Mn between the charged and discharged Mn in ironmaking sector was considered to be discharged from the system in the form of scrap and dust.

3.2. Manganese Flow in the Steelmaking Process

The production of crude steel in Japan was 112.5 × 10^6 t in 2005. The amount of steelmaking slag generated during the production of crude steel was calculated as 13.7 × 10^6 t. This calculation was based on the amount of basic oxygen furnace (BOF) slag and the electric arc furnace (EAF) slag per unit crude steel production, as published by the Nippon Slag Association. Because the values in the calendar year 2005 were not available, the values in the fiscal year 2005 (0.121 t of BOF slag and 0.123 t of EAF slag) were used for the calculation.

Figure 6 shows the calculation procedure for the Mn flow in the steelmaking process. In the steelmaking process, crude steel is produced as the main product and steelmaking slag is generated as a by-product in a BOF or an EAF. The composition of steelmaking slag varies significantly with the type of manufactured steel. Therefore, this study calculates the Mn content in steelmaking slag from the material balance of the Mn in the steelmaking process. In other words, the Mn content in the steelmaking slag was calculated by subtracting the Mn content in the crude steel from the amount of charged Mn, which was derived from the raw materials.

The Mn content in the crude steel was calculated from that in the steel products. The Mn content in the steel products was calculated by classifying the ordinary steels into 8 types of steel and special steels into 13 types of steel on the basis of the report compiled by the Steel Recycling Research Co., Ltd. As a result of this calculation, the weighted average of the Mn content in the steel products per ton were 0.42% for ordinary steel products and 0.91% for special steel products. From this result, the Mn content in crude steel in 2005 was 590.3 × 10^3 t-Mn of which the Mn content in ordinary steels was 367.4 × 10^3 t-Mn and that in special steels was 222.9 × 10^3 t-Mn.

The major sources of Mn in the steelmaking process are the above-mentioned pig iron, scrap, metal Mn, Ferro-Mn, Si–Mn, Mn ore, and ferruginous Mn ore. The consumption of Ferro-Mn and Si–Mn for crude steel manufacturing were based on the statistics compiled by METI, and the consumption of metal Mn were based on the data compiled by

Table 1. Background data for the estimation of Mn flow.

| Material          | Mn content (%) |
|-------------------|----------------|
| Pig iron          | 0.25           |
| Iron ore          | 0.20           |
| Iron-Mn ore       | 0.30           |
| Scrap             | 0.25           |

Fig. 5. Mn flow in the ironmaking process (2005).

Fig. 6. Flow chart for the estimation of Mn flow in the steelmaking process.
The Mn content in these raw materials were also based on the data compiled by JOGMEC. The consumption of Mn ore and ferruginous Mn ore in the steelmaking process during and after 2004 were not obtained from the statistics compiled by METI due to downsizing of the statistics.

For this reason, the ratio of the consumption of Mn ore or ferruginous Mn ore to crude steel production was calculated from the data compiled by METI in 2003 and used as coefficients. The Mn content in Mn ore was assumed to be 39.00% because most of the Mn ore imported into Japan was the Mn ore in which the Mn content was 39% or more (HS code: 260200-012). The Mn content in ferruginous Mn ore per ton was assumed to be 30.14% from our survey.

Figure 7 shows the Mn flow in the steelmaking process in 2005. Manganese metal (Metal Mn), which is mainly imported from China, is used as an additive in the manufacturing of steel in order to develop hardness, wear resistance, and corrosion resistance. It is an indispensable material in the steel industry. The calculation revealed that 543.4 t-Mn was charged in the primary refining process as ferrous raw materials and additives and 577.6 t-Mn was charged in the secondary refining process as Ferro-Mn, Si–Mn, and metal Mn. On the other hand, the Mn content in crude steel was 590.3 t-Mn, as mentioned above. Therefore, from the material balance in the steelmaking process, it was calculated that 530.7 t-Mn was discharged as steelmaking slag.

3.3. Manganese Flow Associated with the Iron and Steel Cycle

The calculated Mn flow associated with the iron resources cycle is shown in Fig. 8. 517.7 t-Mn was discharged as steelmaking slag including hot metal pretreatment slag in the current iron and steelmaking process. This Mn originated from the iron ore and a part of the additives. On the other hand, it was found that 577.6 t-Mn was charged as Ferro-Mn and so on in order to compensate for the Mn discharged as steelmaking slag.

4. Discussion

This chapter discusses (a) the adequacy of our calculation and (b) the possibility for the effective use of Mn in slag.

The composition of BF slag is uniform; however, the composition of steelmaking slag is considered to vary significantly according to the target steel type, treatment process, and refining facility. Since it is difficult to obtain individual pieces of information about the composition of slag in each factory, this study estimated the amount of Mn oxidation loss into the steelmaking slag by subtracting the Mn discharged into the steel products from the charged Mn, including the ferroalloy and pig iron manufacturing processes. In this chapter, the calculations are verified with regard to the composition of steelmaking slag presented by the Nippon Slag Association.

According to statistics reported by the Nippon Slag Association, the MnO content in the BOF slag per ton was 5.3 t-MnO. The MnO content in two types of EAF slag per ton were 7.9 t-MnO in the oxidized slag and 1.0 t-MnO in the reduced slag. The median value of 4.45 t-MnO was used as the MnO content in the EAF slag because the individual values of the generated slag in the two types of EAF slag were not obtained. From the calculation of the slag composition and the amount of generated steelmaking slag, the total Mn content in the steelmaking slag was obtained as 537.7 t-Mn of which the Mn content in the BOF slag was 415.4 t-Mn and that in the EAF slag was 122.3 t-Mn. The figures obtained in this chapter closely approximate our calculations in this study. Therefore, it can be considered that our calculations nearly reflect the Mn flow in the steelmaking process.

The authors have proposed the processes of magnetic separation and recovery of phosphate-rich crystalline phase from slag by utilizing the differences in the magnetic properties of the precipitated crystalline phases in the steelmaking slag. The properties of precipitated phase such as composition, grain size, and crystal structure are significantly influenced by the total composition of the slag and cooling conditions. It is indicated that Mn exhibits significant segregation under some conditions. As determined in this study, the amount of oxidation loss of Mn into steelmaking slag was nearly equal to that of the charged Mn as a form of ferroalloy for alloying and deoxidizing. Therefore, if the Mn-rich phase segregation in slag can be recovered by some processes, a significantly large ripple effect can be expected as in the case of the separation and recovery of phosphorus.

5. Conclusions

1. It was revealed that Mn charged as iron ore and the...
Mn content of other ferrous raw materials reached \(266.2 \times 10^3\) t-Mn of which \(208.9 \times 10^3\) t-Mn was discharged as pig iron and \(55.4 \times 10^3\) t-Mn as blast furnace slag in the ironmaking process.

(2) It was observed that in the steelmaking process, \(530.7 \times 10^3\) t-Mn was discharged as steelmaking slag and \(577.6 \times 10^3\) t-Mn was charged in the secondary refining process as Ferro-Mn, Si–Mn, and metal Mn for the purpose of adding them as constituents of alloy.

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REFERENCES

1) Japan Oil, Gas and Metals National Corporation: Stockpiling, (http://www.jogmec.go.jp/english/activities/stockpiling_metal/index.html), (2007/8/1).
2) Ministry of Economy, Trade and Industry: Yearbook of Iron and Steel, Non-ferrous Metals, and Fabricated Metals Statistics, (2006).
3) Japan Oil, Gas and Metals National Corporation: Material Flow of Mineral Resource 2005 (in Japanese), (2006).
4) Rare Metal Association: Rare Metals Shikihou (in Japanese), (2007).
5) M. Shimada, K. Ijima, Y. Sawatani, K. Nakajima, T. Nagasaka, T. Tsukihashi, Y. Moriguchi and K. Halada: New Trend of Material Flow in the Era of Globalization, Advances in Ecomaterials (Proc. of 7th Int. Conf. on Ecomaterials), Stallion Press, Singapore, (2005), 620.
6) P. H. Brunner and H. Rechberger: Handbook of Material Flow Analysis, The CRC Press, Boca Raton, (2003), 1.
7) M. Bertram, T. E. Graedel, H. Rechberger and S. Spatari: Ecol. Econ., 42 (2002), 43.
8) H. Rechberger and T. E. Graedel: Ecol. Econ., 42 (2002), 59.
9) S. Bringezu, H. Schutz, S. Steger and J. Baudisch: Ecol. Econ., 51 (2004), 97.
10) S. Nakamura and K. Nakajima: Mater. Trans., 46 (2005), 2550.
11) K. Nakajima and S. Nakamura: J. Jpn. Inst. Met., 70 (2006), No. 8, 618.
12) K. Nakajima, K. Yokoyama, Y. Matsuno and T. Nagasaka: ISIJ Int., 47 (2007), No. 3, 510.
13) K. Nakajima, H. Osuga, K. Yokoyama and T. Nagasaka: Mater. Trans., 48 (2007), No. 8, 2219.
14) K. Nakajima, K. Yokoyama, K. Nakano and T. Nagasaka: Mater. Trans., 48 (2007), No. 9, 2365.
15) H. Minami: Met. Resour. Rep. (in Japanese), JOGMEC, 36 (2007), No. 5, 846.
16) Japan Oil, Gas and Metals National Corporation: Material Flow of Mineral Resource 2006 (in Japanese), (2007), 73.
17) Ministry of Economy, Trade and Industry: Yearbook of Iron and Steel, Non-ferrous Metals, and Fabricated Metals Statistics, (2007), 215.
18) Arumu Publishing: Industrial Rare Metals 121 (in Japanese), (2005), 92.
19) International Iron and Steel Institute: Steel Statistic, (http://www.worldsteel.org/?action=archivedsteellist2), (2007/8/1).
20) The Japan Ferrous Raw Materials Association: Year Book of Ferrous Raw Materials (in Japanese), (2006), 10.
21) Nippon Slag Association: Iron and Steel Slag (in Japanese), (2006), 11.
22) Nippon Slag Association: Chemical Composition of Iron and Steel Slag, (http://slg.jp/slag/slag-seisitsu.htm), (2007/8/1).
23) Steel Recycling Research: Supply and Demand of Manganese, (2007), 19.
24) Ministry of Economy, Trade and Industry: Yearbook of Iron and Steel, Non-ferrous Metals, and Fabricated Metals Statistics, (2007), 39.
25) K. Yokoyama, H. Kubo, K. Mori, H. Okada, S. Takeuchi and T. Nagasaka: ISIJ Int., 47 (2007), No. 10, 1541.
26) K. Nakajima, K. Yokoyama, S. Hayashi and T. Nagasaka: CAMP-ISIJ, 20 (2007), 919.