Removal of Mn, Nb, V and P from Iron Ore using Iron and Steelmaking Processes

Ryo Inoue, Shigeru Ueda, Tatsuro Ariyama

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

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ABSTRACT

Some rare metal elements such as Mn, Nb and V are contained along with P in iron ore. As a resource strategy in Japan, the possibility of efficient recovery of these elements as byproducts of steel in conventional iron and steelmaking processes has been discussed. It was clarified that rare metals can be easily transferred to molten pig iron in a blast furnace, and to steelmaking slag in a hot metal pretreatment and an oxygen blowing furnace. Rare metals were concentrated in specific mineral phases during the cooling and solidification of the steelmaking slag. The separation of the phases containing higher contents of rare metals from other phases is considered to be a key-point in order to obtain a higher quality ore substitute.

Keywords: rare metal, phosphorus, recovery, by-product of steel.

1. INTRODUCTION

A stable supply of resources and energy from foreign countries are indispensable in the steelmaking industries and Hi-tech industries of Japan. However, due to the unstable variations in resource prices caused by resource hunting, resource nationalism and the influence of major resource companies, the resource strategy in stockpiling and trade is becoming a national issue. It is well known that the supply of rare metals is controlled by the main production countries. Although almost of all natural resources have been imported for economic progress in Japan, the long-term resource strategy is seriously insufficient compared with the American and European nations. It is extremely important from the viewpoint of resource strategy to develop the new technology for the recycling of rare elements and the substitution with general elements, which is not influenced by external factors.

According to Rare Metals Handbook /1/, a rare metal is defined as having one of the following characteristics.

1. The amount of element in the Earth's crust is limited, and the supplied amount of natural ore is limited.
2. The content of the element in ore deposites is too low to operate economically.
3. The substitution for another pure element is hard because of the specific physicochemical properties.
4. Its economical advantage is superior to other materials.

Recently, the following characteristics are also supposed in the definition of a rare metal.

5. The amount in the earth's crust is limited and the element is unevenly distributed
6. The element is included in other mineral ore at a low concentration.

7. The refining is technically difficult and the refining cost is high.

Based on the national resource policy of the Japanese government, the stock of 7 elements (Ni, Cr, Mn, W, Co, Mo and V), whose substitution with other elements is scarce and the segregation of ore is remarkable in the world, have been carried out by JOGMEC since 1983. In the U.S.A., 17 metallic minerals are stocked as a strategic stockpile by the Department of Defense, and 11 elements are stocked as economic security savings in China. The 7 elements stocked in Japan are mainly used in stainless and special steelmaking processes.

Some rare metal elements, such as Mn, Nb and V are contained along with P in the iron ore, are steadily imported depending on the efforts of the steelmaking industry. Therefore, it is extremely preferable for the resource strategy that these elements are efficiently obtained as byproducts of steel. In the present study, the utilization of rare metals in the steelmaking process is described. Then, the possibility of recovery of rare metals and phosphorus using conventional iron and steelmaking processes will be discussed.

2. UTILIZATION OF RARE METALS

2.1. Advanced usage of rare metals in the steelmaking process

A stable supply of Nb and Ti is also required by steelmaking companies along with the 7 elements mentioned above. The effects of these elements on steel properties are listed in **Table 1**. As shown in this table, lighter automobiles, higher tension of welded slabs and higher oxidation resistance of ferric stainless steel could be obtained by the development of IF (Interstitial Free) steel, HSLA (High-strength Low-alloyed) steel, DP (Dual Phase) steel and TRIP (Transformation Induced Plasticity) steel.

Functions of rare metals in these steels by Imagunbai /2/ are as follows: In the case of IF steel, the productivity and accuracy of press shaping can be improved by controlling the concentration of Nb or Ti related to that of C and N. In HSLA steel, the addition of small amounts of Nb, V, Ti and Mo increase the strength of hot rolled steel sheets. The press performance, profile accuracy and resistance to fatigue of DP steel and TRIP steel are improved compared with HSLA steel. In these steels, a critical structure control using rare metal such as Nb has been used by controlling the heat history during the hot rolling, cooling and coil winding processes.

The mechanical characteristics obtained by the addition of the alloying elements including rare metals has been used in steel plates for shipbuilding, buildings and line pipes. It is known that carbon is most harmful for the welding performance (weldability and toughness of the welded point) though steel strength is obtained by increasing the carbon content. Therefore, carbon concentration is limited below 0.1 mass% in thick high-tensile strength steel plates, whose strength, low-temperature toughness, and toughness of welding heat affected zone (HAZ) could be compensated by the addition of Mn, Si, Ni, Mo, Cr, V, Nb, Ti and so on. Although these elements also deteriorate the welding performance, the effects other than strength such as low-temperature toughness, oxidation-resistance, etc. are obtained by their addition. The amount of those elements is determined by considering the carbon equivalent weight, $C_{eq.}$ ($C_{eq.}$= [mass% C]+[mass% Mn] /6+([mass% Ni]+[mass% Cu])/15+ ([mass% Cr]+[mass% Mo]+[mass% V])/5 for instance) in the concentration range where the minus to the welding performance can be allowed.

When a large amount of Cr and Ni are used in stainless steel, it is called austenitic stainless steel. Recently, stainless steel not containing Ni, which is called ferritic stainless steel, has been used for the exhaust systems of cars and motor vehicles. Ferritic stainless steel has also come to be used also for buildings and durable consumer goods. In this stainless steel, Nb or Ti are used above 0.5% for resistance to oxidation at high temperature.

2.2. Use of rare metals in frontier industries

A lot of rare metals other than the seven elements, which have been stocked by JOGMEC based on the Japanese saving policy, are indispensable to high technologies such as cars, electricity, electronics, airplanes and space crafts, and are listed in **Table 2**. The

Table 1

Main usage of rare metals and their effects on steel properties

Rare metal	Main usage	Effect on steel properties
Ni	Stainless steel, Nonferrous alloy	Heat resistance Abrasion resistance
Cr	Stainless steel, Nonferrous alloy	Anti-corrosion Abrasion resistance
Mn	Steel	Toughness Thermal refining of steel
W	Super-hard alloy, High-pressure circuit of engine, Munitions	Heat resistance Abrasion resistance
Co	Magnet, Heat resistant alloy, Super-hard alloy	Heat resistance, Toughness Anti-corrosion
Mo	Stainless steel, Nonferrous alloy, Electrode, Filament, Heat shield, Lubricant	Heat resistance
V	Cutting tool	Toughness
Nb	Steel, Stainless steel, Super-hard alloy, Piezoelectric element, Capacitor	Heat resistance, Toughness Anti-corrosion, Impact-proof
Ti	Steel, Stainless steel, Heat resistant alloy, Super-hard alloy, Anti-corrosion construction material	Toughness, Heat resistance, Anti-corrosion

Table 2

Main usage of rare metals in frontier industry and their alternative element

Rare metal	Main usage in frontier industry	alternative element
Ta	Capacitor	Al, Nb, Ceramics
	Super hard tool	Nb
	Optical glass, Filter for electronic equipment	
Sr	Ferrite magnet, Capacitor	
	Cathode-ray tube	Ba
Ga	Light emitting diode, Semiconductor laser	
	Solar battery	Si
In, Sb, Sn	Transparent electrode	(ZnO, SnO)
Dy, Nd, Sm	Rare earth permanent magnet	
Pt	Exhaust gas catalyst	Pd, Mo-Al_2O_3

alternative elements clarified by recent research are shown in the same table.

Phosphorus is not contained in the rare metal group but it is indispensable to fertilizer, chemical industrial goods, medicine, surface treatment of steel sheets and fuel cells. Therefore, phosphorus ore is considered to be of importance by specification for the export prohibition goods in the United States. The phosphorus ore segregates regionally.

3. CIRCULATION OF RARE METALS IN THE IRON AND STEEL INDUSTRIES

3.1. Recycling of rare metals

Waste exhausted during the production of appliances and electronic items, used appliances and used electronic items, and steel scrap are generated daily. They are called urban mines due to the high content of the rare metals. However, the recycling of rare metals doesn't work out as a business, because the concentration of rare metals is a little (or it is not clear) excluding the elements with high concentrations (Ni, Cr) in stainless steel scrap and the other condensed elements in high alloy steel.

Based on the report supervised by the Agency of Natural Resources and Energy /3/, the material flow of rare metals in Japan are summarized as follows:

The annual consumption of Mn in the productions of steel and batteries are 550,000 and 25,000 tons, respectively. Recycling of Mn is hardly carried out because the import prices of virginal Fe-Mn alloy and Mn ore are comparatively low. Used batteries are abandoned as general garbage and nonflammable waste.

The annual consumption of W is 63000 tons (2005). 58% of W is used for high-speed tool steels which need high levels of hardness, abrasion resistance and are heatproof. The special steel production consumes 19% of W. 17% of W is used for metal products such as illuminators, electronic parts and electric parts. The quantitative statistics of the W amount in steel scrap have not been reported. It was presumed in 2005 that 1100 tons of W contained in home scrap were changed to steel in special steel plants. Although 30% of marketed hard tool materials are collected, the majority are being exported because there are only a few recycling facilities in Japan.

15,000 tons/year of Co are used for the positive pole material of rechargeable batteries, the magnetic materials and the metallic materials such as super-alloys, special steels, etc. 64% of Co is consumed through batteries, 16% for magnetic materials, and 7% for special steels and tool steels. Almost all used batteries are exported to Canada and China because the recycling facilities are few and the usage of reproduced Co has been limited in Japan. It was reported in 2005 that 400 tons Co contained in home scrap were changed to steel in steel plants.

In the case of V, 90% of the annual consumption of 5,600 tons is used for steelmaking. The V content is 1.75 mass% in high-tensile steel and 4.2~5.2 mass% in high-speed steels. These steel scraps are dissolved not alone, but with other low V steels. Therefore, the V content in the slag obtained by the conventional refining process is too low to recover V from those slags technically and economically.

The annual consumption of Nb is 7,200 tons, and is mostly used for steelmaking. Nb is called the rare metal with the most strict nationalism over resource. Since 90% of the Nb ore supplied to the world is mined by Araxá in Brazil, an uneasy supply is feared in the future. The Nb content in slag obtained by the conventional refining process is too low to recover Nb from those slags technically and economically.

It is known that some rare-earth metals can be recycled technically, but they are hardly recycled due to the high recycling cost and small commercial market of rare-earth metals.

Generally, the recovery of rare metals from scrap and waste has not been examined thoroughly despite the uneasy supply of rare metal ores in the future, because the concentration of rare metals in scrap and waste is lower than the cost advantage of commercial recycling. In the present material flow in Japan, most wastes containing the above mentioned rare metals are exported or abandoned.

On the contrary, Ni, Cr and Mo have been recycled positively. The Ni price rose suddenly due to the ore supply trouble because of the strike by mine workers and smelters several times, and due to the rapid increase in austenitic stainless steel demand and the speculation object for Ni in 2006. The annual Ni consumption in Japan was 230,000 tons in 2005. 67% of Ni is used for stainless steel and special steels, and 30% in industries related to Information-technology (IT). It was announced that 44% of the total consumption of domestic stainless steel and special steels was added to steel as scraps (home scrap, city scrap and imported alloy scrap).

The supply trouble of Cr had been caused by the internal troubles of mining and refining companies, natural damages and the supply troubles by the production adjustment. Cr consumption in Japan was 1.03 million tons in 2005, and most was used for stainless steel and special steels. It was reported that 26% of the total consumption of domestic stainless steel and special steels was added to steel as scraps (home scrap, city scrap and imported alloy scrap).

Mo is an important element for improving the strength, corrosion resistance, and toughness of steel as well as Ni and Cr. More than 80% of the annual Mo consumption, which was 28,000 tons in 2005, was used for steelmaking. The recycled amount of Mo in the steelmaking process is estimated to be 19% (5,200 tons) as a Mo amount contained in in-house generated rubbish and external buying rubbish.

3.2. Recovery of rare metals contained in iron ore

A long-term stable supply of iron ore has been established by the efforts of the steelmaking companies in Japan. Some rare metal elements (Mn, Nb, V) are contained in iron ore along with phosphorus as shown in **Table 3**. Therefore, it is extremely effective for the resource strategy of our country when these rare metals and phosphorus can be recovered as a by-product of steel. In this section, the possibility of recovery of rare metals and phosphorus contained in iron ore will be examined on the basis of the reduction in ironmaking and the refining in the steelmaking process.

Table 3

Iron ore containing a large amount of rare metal elements

Iron ore	High concentration of rare metal
Savage River (U.S.A.)	0.46 mass% V
Taharoa (New Zealand)	0.30 mass% V, 0.50 mass% Mn, 0.17 mass% P
Panzhihua (China)	0.21 mass% V
Algabo (Argentina)	0.19 mass% V
Arado Lake (Canada)	0.14 mass% V
Kiruna (Sweden)	0.10 mass% V, 1.5 mass% P
Baotou (China)	0.28 mass% Nb, 0.41 mass% P
Erzberg (Indonesia)	1.8 mass% Mn
India (India)	0.71 mass% Mn
Mesabi (U.S.A.)	0.45 mass% Mn
Shaffer Bill (Canada)	0.43 mass% Mn
Göttingen (Germany)	0.36 mass% Mn, 1.0 mass% P
Yorkshire (England)	0.33 mass% Mn, 0.63 mass% P
Lorraine (France)	0.28 mass% Mn, 0.82 mass% P
MBR (Australia)	0.25 mass% Mn
New Caledonia (France)	0.67 mass% Ni, 2.4 mass% Cr

When the recovery of rare sources is carried out using the process shown in **Figure 1**, the behavior of rare metals and phosphorus at each stage is explained as follows:

1. By the carbon reduction of iron ore, which contains valuable elements voluminously, those elements are transferred to the molten pig iron.
2. The valuable elements (Nb, V, P and Mn) in the molten pig iron are transferred to slag by the oxidizing reaction through hot metal pretreatment and BOF processes.
3. The valuable elements in slag are concentrated in a specific mineral phase during the cooling and solidification of the slag, and the mineral phases are separated from the others.

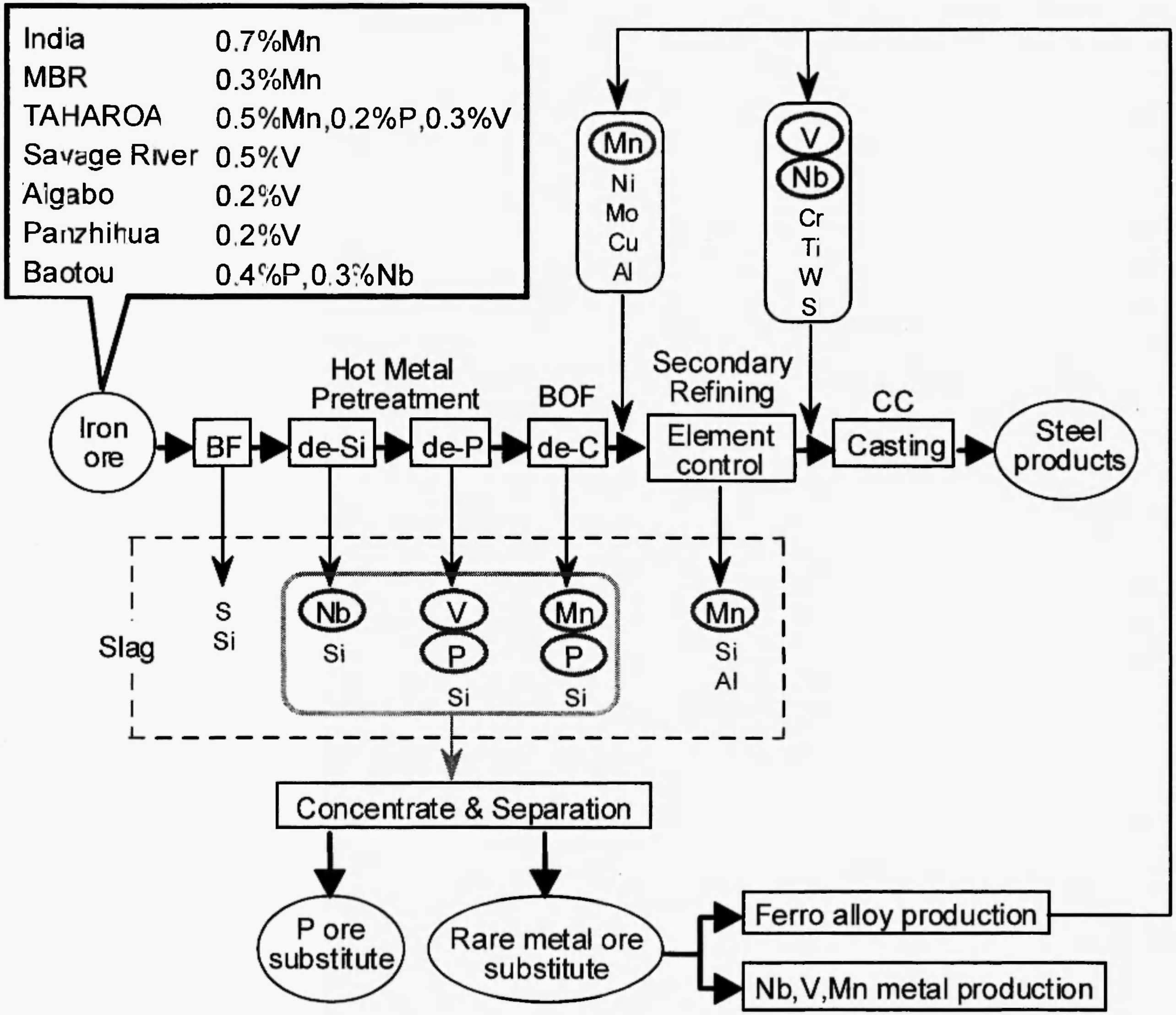

Fig. 1: Schematic diagram of rare metal recovery using conventional iron and steelmaking process

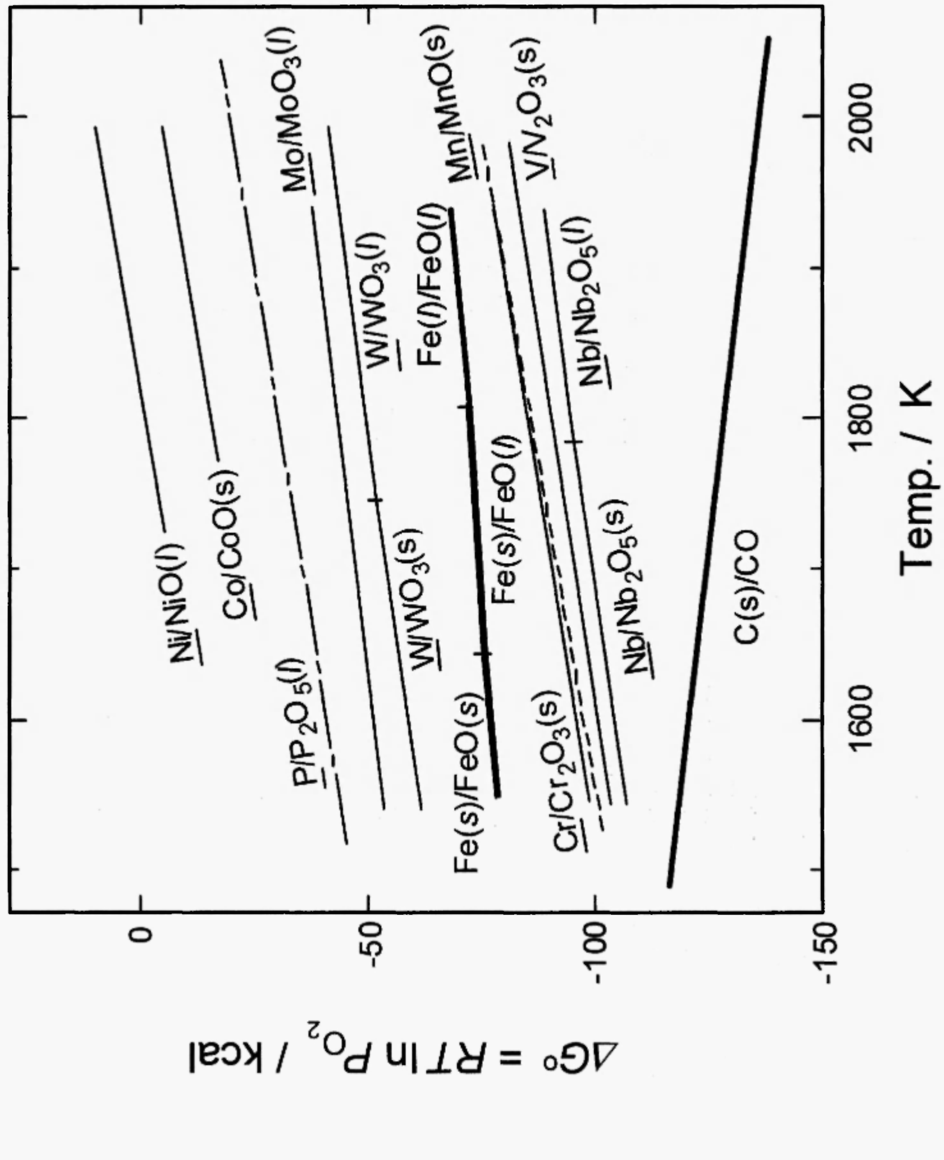

Fig. 2: Relations between free energy of M/M$_{x/2}$O equilibrium and temperature

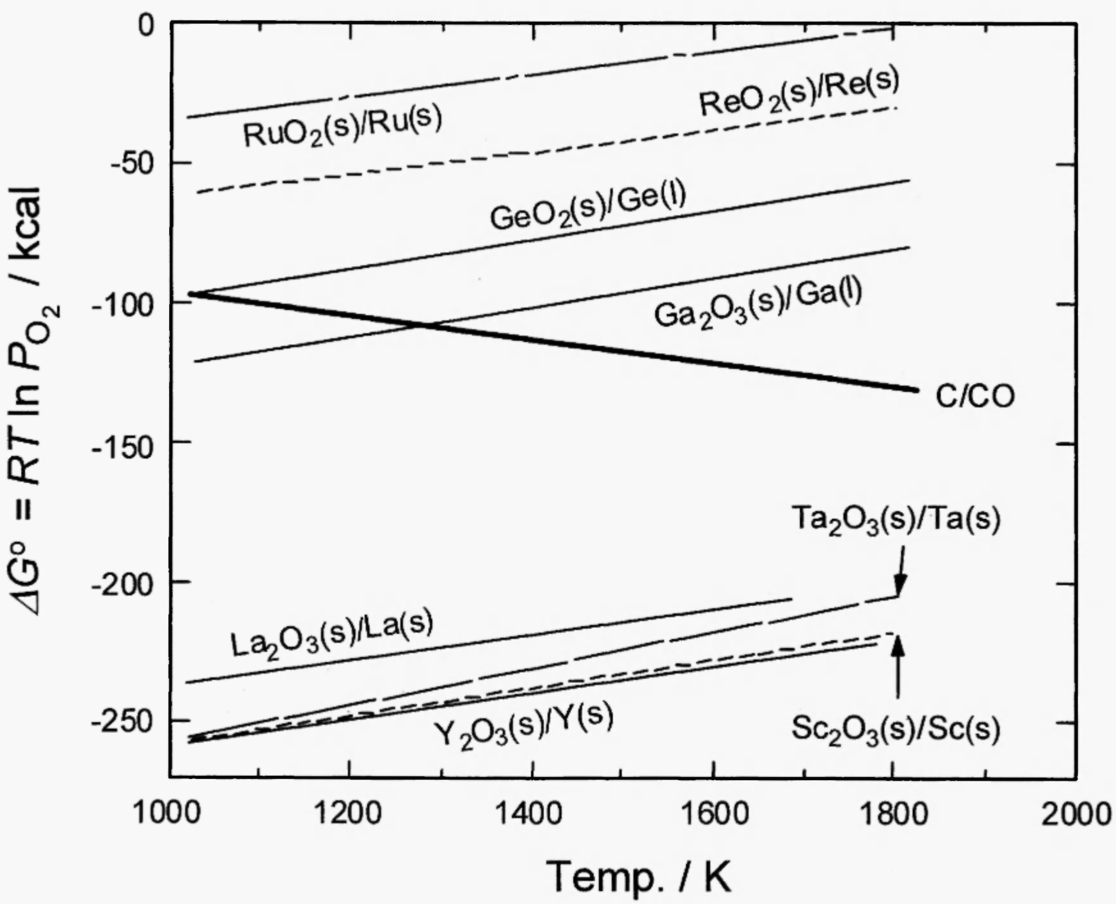

Fig. 3: Free energy of formation of rare earth metal oxide plotted against temperature

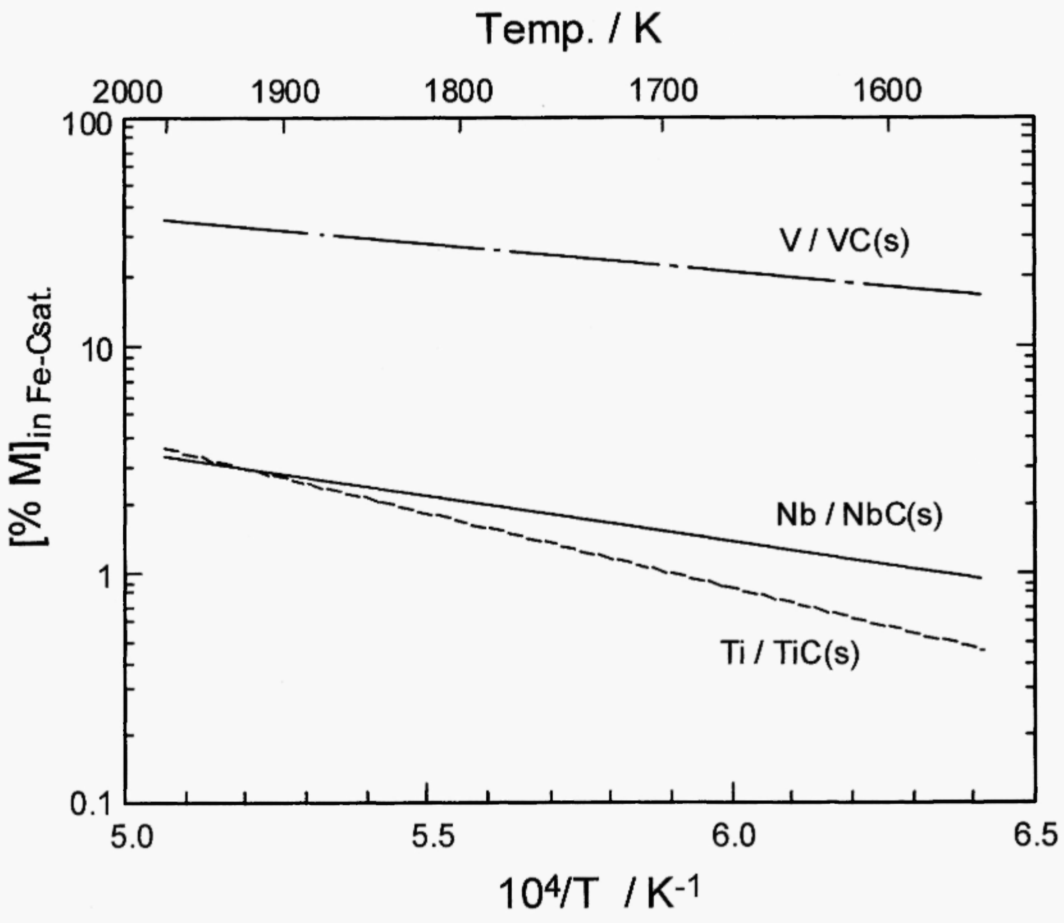

Fig. 4: Temperature dependence of the content of M (M= Nb, Ti, V) in carbon-saturated iron melt equilibrated with its carbide.

4. The ferroalloy is manufactured by using the mineral phase containing large amounts of value elements. The obtained ferroalloy is used in the steelmaking process. The mineral phase concentration of the rare metal is supplied to other industries as a high-quality rare metal ore. The concentrated phosphorus is supplied as a substitute for phosphorus ore.

3.2.1. Reduction of rare metal oxides contained in iron ore

The possibility of the reduction of rare metal oxides with carbon, which is a usual reducing agent in the ironmaking process, was examined using thermodynamics data /4-9/. Relationships between the free energy of the reaction [1] and temperature are given in **Figure 2**.

$$2M_{x/2}O = x[\underline{M}] \text{ (in molten iron, 1mass\% standard)} + O_2 \quad [1]$$

The rare metal oxides in the upper part of the C/CO equilibrium line /5,6/ are able to be reduced by C according to reaction [2], thus resulting that rare metals easily dissolve in iron.

$$2M_{x/2}O + 2C(s) = x[\underline{M}]\text{(in molten iron, 1mass\% standard)} + 2CO \quad [2]$$

Since the free energy of the dissolution reaction, M(s, l) = M(in molten iron, 1mass% standard), is not reported concerning rare earth metal, the relationships between the free energy of the reaction [3] and temperature are given in **Figure 3**.

$$2M_{x/2}O = xM(s, l) + O_2 \quad [3]$$

The rare earth metal oxides in the upper part of the C/CO equilibrium line, such as Ga_2O_3, GeO_2, ReO_2 and RuO_2, can be reduced by C.

However, each line is derived at the standard state of M, M and $M_{x/2}O$ in **Figures 2** and **3**. When the activity of $\underline{M}$ or M became lower, reaction [2] or [3] proceeded to the right hand side because the corresponding line shifted to the upper part of **Figure 2** or **3**. When the activity of MO became lower, the corresponding line shifted to the lower part of **Figure 2** and **3** and the reduction by C became difficult. Tsukihashi et al. /10/ reported that the distribution ratios of V and Mn between $CaO\text{-}SiO_2\text{-}CaF_2$ slag and carbon-saturated iron melts were 0.4 and 2 at 1573 K, respectively. Han et al. /11/ showed that the Nb distribution ratio between $CaO\text{-}SiO_2$-5 mass% $Al_2O_3\text{-}CaF_2$ slag and carbon-saturated iron melt was 0.03 at 1673 K. It is expected that the distribution ratios of V, Nb and Mn between $CaO\text{-}SiO_2\text{-}Al_2O_3$ blast furnace slag and molten pig iron become lower than those reported values. Almost all amounts of these elements will be included in the molten pig iron after the reducing reaction in blast furnace.

3.2.2. Formation of rare metal carbide

When iron ore with a high Ti content is reduced by coke in the ironmaking process, the TiC layer is observed on a blast furnace hearth. Along with this phenomenon, when rare metal carbides precipitate on carbon bricks or coke after the reaction between carbon and the rare metal have dissolved in the molten pig iron, the rare metals as carbide are not transferred to the next oxidation stage. To prevent the loss of rare metals caused by carbide formation, it is important to know the solubility of rare metals in pig iron. The possibility of carbide formation was examined by using thermodynamic data. In a NbC formation reaction [4] in which the Nb in a carbon-saturated iron melt reacts with solid C, the temperature dependence of Nb content is expressed by Equation [5] /12/.

$$[Nb] + C(s) = NbC(s) \quad [4]$$

$$\log [\text{mass\% Nb}] = -3980/T + 2.53 \quad [5]$$

As a comparison, the TiC usually observed in a blast furnace hearth forms after reaction [6]. The temperature dependence of Ti content in a molten iron double-saturated with carbon and TiC is expressed by Equation [7] /13/.

$$[Ti] + C(s) = TiC(s) \quad [6]$$

$$\log [\text{mass\% Ti}] = -6760/T + 3.965 \quad [7]$$

The relationship between the content of Nb and Ti in a carbon saturation molten iron saturated with NbC and TiC, respectively, and reciprocal of absolute temperature are shown in **Figure 4** by using Equations [5] and [7]. It can be found from this figure that the loss of these metals by carbide generation can be prevented when neither Nb nor Ti exceeds 1 mass% above 1773 K.

The V content in a carbon saturation molten iron saturated with VC, which had not been reported previously, is estimated as follows: Equation [8] describes the VC precipitation reaction. The temperature dependence of V content in molten iron is expressed by Equation [9] using the activity coefficient of V, $f_{[V]}$.

$$[V] + C(s) = VC(s) \qquad \Delta G^{\circ} = -19450+13.2T \text{ (cal)} \quad /4,5/ \qquad [8]$$

$$\log\,[\text{mass\% V}] = -4251/T + 2.89 - \log f_{[V]} \qquad [9]$$

where $f_{[V]}$ is expressed by Equation [10] using the respective interaction parameters, $e_V{}^i$, $r_V{}^i$ and $r_V{}^{V,i}$.

$$\log f_{[V]} = e_V{}^i[\text{mass\% } i] + r_V{}^i\,[\text{mass\% } i]^2 + r_V{}^{V,i}\,[\text{mass\% V}]\cdot[\text{mass\% } i] \qquad [10]$$

The saturated carbon content in an iron melt is evaluated by Equation [11] /14/, where the m_i listed in **Table 4** is the parameter which indicates the effect of a third element, i, on the carbon solubility of iron /14-16/.

$$[\text{mass\% C}]_{\text{sat.}} = 1.30 + 0.00257(T\text{-}273) + \Sigma m_i[\text{mass\% } i] \qquad [11]$$

Table 4

The parameter m_i which indicates the effect of third element i on the carbon solubility in iron /14-16/

i	m_i	Range	i	m_i	Range
Al	-0.25	< 2 mass% Al	Sb	-0.115	< 15 mass% Sb
Si	-0.317	< 5.5 mass% Si	Ti	+0.14	estimated
P	-0.33	< 3 mass% P	V	+0.135	< 3.4 mass% V
S	-0.36	< 0.4 mass% S	Cr	+0.063	< 9 mass% Cr
Co	-0.026	< 40 mass% Co	Mn	+0.027	< 25 mass% Mn
Ni	-0.053	< 8 mass% Ni	Zr	+0.075	estimated
Cu	-0.074	< 3.8 mass% Cu	Nb	+0.05	estimated
Sn	-0.11	< 4.5 mass% Sn	Mo	+0.025	< 2 mass% Mo

To calculate easily, only the effect of carbon is considered. As the first order interaction parameter, $e_V{}^C$, was only reported at 1873 K [5)], the temperature dependence of $f_{[V]}$ is calculated by approximating a regular solution. Finally, the V content in molten iron saturated with VC and C is expressed by Equation [12].

$$\log\,[\text{mass\% V}] = -4048/T + 3.76 + 45.8[\text{mass\% V}]/T \qquad [12]$$

However, a solution of nonlinear equation [12] was not obtained. Raghavan /17/ showed the Fe-C-V phase diagram by the calculation based on the results by Oya /18/. Based on Raghavan's diagram, the temperature dependence of the V content in molten iron saturated with VC and C is calculated as shown in **Figure 4**. It was found that the V content is so high that VC does not substantially precipitate in molten pig iron.

3.2.3. Oxidation of rare metals in iron melts

The oxidation of rare metal in iron melts by FeO is discussed using thermodynamics data /4-9/. The relation between the free energy of the reaction $2Fe(l)+O_2=2Fe_tO(l)$ ($\Delta G^{\circ}=-111{,}500 + 21.94T$ (cal) /5,8/) and temperature is shown in **Figure 2**. Since it was concluded that the metal, M, whose $\underline{M}$ $/M_{x/2}O$ equilibrium line was in the lower part of Fe/FeO line, is oxidized by FeO, the rare metals, such as V, Nb, and Cr, are inevitably moved from the molten iron to slag in the conventional steelmaking process. This means that the preservation of those rare metals in iron melts is hard in the usual process. However, each line in **Figure 2** was obtained at the standard state of $\underline{M}$ and $M_{x/2}O$, as mentioned in 3.2.1. When the activity of MO became lower, reaction [1] proceeded to the left hand side because the corresponding line shifted to the lower part of **Figure 2**. When the activity of $\underline{M}$ became lower, the corresponding line shifted to the upper part of **Figure 2**, and the oxidation of $\underline{M}$ became difficult.

Marukawa et al. /19/, Inoue and Suito /20/, and Werme and Åström /21/ charged Na_2CO_3 or CaO-Fe_tO flux into molten pig iron containing V, and found that the prior oxidation proceeded in the order of Mn to V to P. Moreover, Inoue and Suito /22/ and Sato et al. /23/ described that the prior oxidation proceeded in the order of Nb to P to Mn in the reaction of the same fluxes with the molten pig iron containing Nb. Yamazaki et al. /24/ investigated the Nb distribution between iron and CaO-SiO_2-Al_2O_3-0.1~6 mass% T.Fe slag at 1823 and 1923 K. They showed that the Nb distribution ratio rapidly increased with increasing slag basicity in T.Fe>2.5 mass%, and it reaches about 100 at (mass% CaO)/(mass% SiO_2) =1. From these results, as well as Mn /25/ and P /26/, the distribution ratio between CaO-SiO_2-Fe_tO slag and molten iron, V, Nb, Mn and P are almost all considered to move to hot metal pretreatment slag.

It is also expected from V /27,28/, Mn /25/ and P /26/ distribution ratios between CaO-SiO_2-Fe_tO-MgO slag and iron melts that V, Mn and P move to BOF slag easily.

3.2.4. Concentration of valuable elements to specific mineral phases in slag

After the observation and quantitative analysis of hot metal pretreatment slag sampled in an actual slag yard, V was concentrated in fluorapatite ($Ca_5F\{(P,V)O_4\}_3$) and dicalcium silicate (Ca_2SiO_4-$Ca_3(P,V)_2O_5$ solid solution) along with P. High content of Mn was observed in the (Mg,Fe^{2+},Mn^{2+},Ca)O-SiO_2 phase. (Ca,Fe)(Nb,Ti,Ta,Zr)O_4 /29/ and $Ca_2Fe_{1.4}Nb_{0.6}O_{5.6}$ /30/ were reported as the mineralogical phase containing Nb in their geology. The concentration of objective elements in specific mineral phases in steelmaking slag, which are varied depending on slag composition and cooling condition, will be discussed in a separate paper .

3.2.5. Separation of the mineral phases containing rare metals from steelmaking slag

After the concentration of those elements to specific mineral phases in steelmaking slag during cooling and solidification, the separation of those phases are required in order to obtain a higher quality ore substitute.

The separation of the $2CaO\cdot SiO_2$ phase, which is the main mineral phase of steelmaking slag, is effective for obtaining rare metals or the condensed phosphorus phase. Ono et al. /31/ found that $2CaO\cdot SiO_2$ particles precipitated as a primary crystal in molten BOF slag could be separated from calcium ferrite using the centrifugal method. Yokoyama et al. /32/ proposed the separation method of calcium phosphate and calcium silicate phases from the Fe oxide-rich phase by using a strong magnetic field. They also reported that the magnetic separation in an aqueous solution was effective /33/.

The ferro alloy containing a large amount of rare metals might be produced after the reaction of the concentrated mineral phases with iron and reducing agents such as Al, Si and C, as can be seen in **Figure 2**. The production of high purity rare metals from concentrated mineral phases will be discussed in a separate paper.

3.2.6. Estimation of the amount of rare metals and P recovered from iron ore

For instance, as 10 million tons of steel a year is manufactured by using TAHAROA iron ore mined in New Zealand (total Fe = 56 mass%) as shown in **Table 3**, 53,000 tons V, 89,000 tons Mn and 30,000 tons P are obtained by assuming the complete recovery of V, Mn and P in the iron ore. The annual demands of V, Mn and P are 10,000 tons, 1.13 million tons and 25,000 tons, respectively, in Japan. Therefore, the amounts of V and P obtained from TAHAROA iron ore fulfill those requirements, while Mn supplies 8% of the quantity demanded. It contributes to the Japanese resource strategy that the steelmaking industries can supply a larger amount of valuable elements as by-products, when they use iron ore containing higher contents of those elements.

4. CONCLUSION

For the construction of a rare metal recovery system using the conventional steelmaking process, it is considered to be efficient that some iron ores containing rare metals are intentionally used as a raw material of a small blast furnace. In this process, rare metals are transferred to pig iron melts in the furnace, and to slag in the hot metal pretreatment and BOF. After the concentration of those elements to specific mineral phases in steelmaking slag during the cooling and solidification, the separation of those phases are required in order to obtain a higher quality ore substitute. A real process will be derived by the basic technologies, which will be established by the examinations of experimental findings and heat and material balance analysis.

The recovery of elements indispensable to frontier industry is not discussed in the present study. Some of those elements are subordinate rare metals, and not present as a single deposit. **Table 5** shows the rare metals contained in main ore. Since these rare metals can be supplied as long as the common metals are produced, it might be considered that the necessity of recycling them is low. However, recycling technologies should be improved against the possibility of a drastic increase in rare metal demand by the development of new technologies.

Table 5

Rare metals coexisted in common metal ore

Main element	Rare metal
Cu	Co, Se, Te, Tl
Zn	Ge, In, Tl
Pb	Sb, Bi
Al	Ga
Mo	Re

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