High Temperature Materials and Processes, Vol. 8, No. 1, 1988, 29-38

Production of High-Purity Niobium by Carbon Reduction Smelting and Electron Beam Melting

Kouji Mimura and Michio Nanjo

Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, 1,1 Katahira, 2-Chome, Sendai, 980, Japan

CONTENTS

ISSN 0334-1704

ABSTRACT

This paper deals with a two-stage heat treatment method in which carbon reduction smelting of niobium oxides and electron beam melting-refining of niobium are combined to produce high-purity niobium. In carbon reduction smelting, Ar plasma arc was used as a heat source, and the relations of carbon mixing mole ratio to Nb_2O_5 (C/Nb_2O_5) to the amounts of oxygen and carbon contents remaining in the reduced niobium were investigated, together with the reduction conditions for enhancing the degassing effect in the subsequent electron-beam melting stage. In the two-stage method, the recovery of niobium was examined as well as the possibility of removing or decreasing metal impurities.

1. INTRODUCTION

Niobium metal is highly heat-resistant, corrosion-resistant and superconductive, so it has found, in the form of pure metal and alloys, increasing applications in structural, electronic and functional materials. These trends require efficient mass-production methods to produce high-purity niobium ingot from the raw material, niobium pentoxide /1-3/.

For reduction of niobium pentoxide, carbon reduction in solid-state in a vacuum at 2,000 K or over is well known, but several hours of heat treatment under a vacuum of about 0.1 Pa to produce niobium with a purity of 99% or more are required /4-6/. Meanwhile, carbon reduction smelting at high temperature above the melting point of niobium (2,740 K) using a plasma arc furnace as a high-temperature heating source allows the reduction reaction to proceed rapidly, /7-9/ resulting in the production of niobium metal in a very short time; accordingly, carbon reduction smelting seems to be a promising continuous mass-production method using large-size furnaces in the future. Electron beam melting of niobium is also considered for deoxidizing by evaporation of niobium suboxides, and also for removing high-vapor-pressure metal impurities by evaporation /1,5,10,11/.

2. EXPERIMENTAL METHODS

The flow sheet for producing pure niobium is given in Fig. 1.

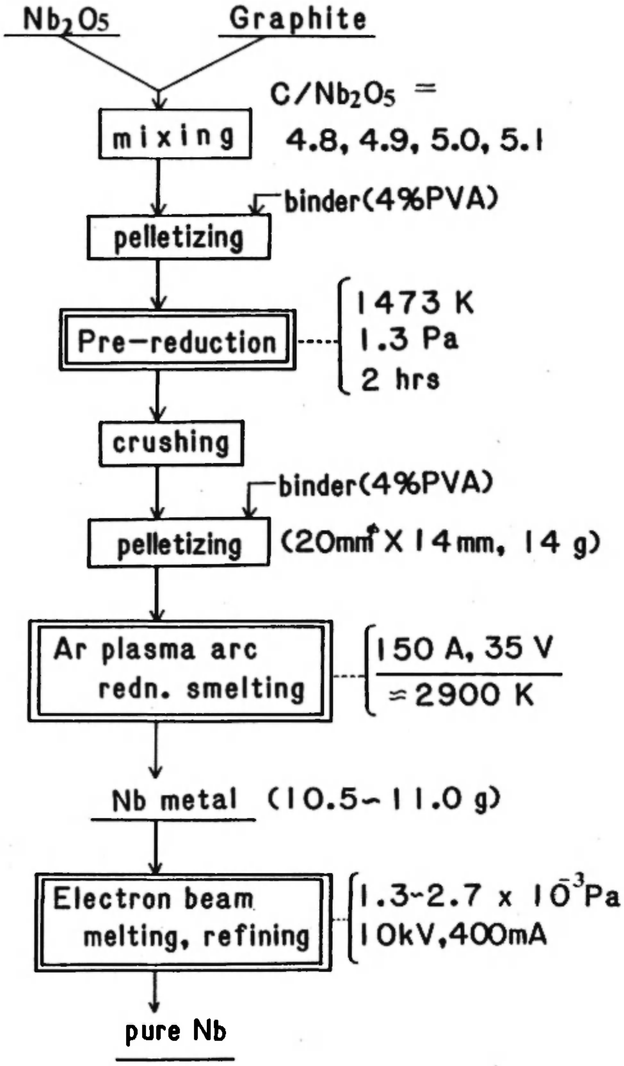

Fig. 1: Flow sheet of production of high purity Nb in the present work.

2.1. Sample Preparation

Table 1 shows the analyses and particle size of Nb_2O_5 and graphite, both of which were used as raw materials. The purity of Nb_2O_5 was above 99.9%, while the graphite contained 98.83% fixed carbon and about 100ppm iron. According to Eq. (1) the stoichiometric mixing ratio of carbon to Nb_2O_5 is 5, but four values, 4.8, 4.9, 5.0 and 5.1 were chosen to examine the effect of the C/Nb_2O_5 ratios.

$$Nb_2O_5 + 5C = 2Nb + 5CO \tag{1}$$

TABLE 1: Analyses of raw materials used in present work.

	Nb_2O_5	Graphite
	(ppm)	(ppm)
Fe	1	100
Al	2	2
Si	15	
Ta	62	
W	15	
Mo	<1	
V	<1	
Ti	17	
Nb_2O_5	>99.9%	—
C	—	98.83%
ash	—	0.11%
size	-325mesh	-325mesh

After Nb_2O_5 and graphite were mixed, about 2 ml polyvinyl alcohol (4%-PVA) as a binder were added to every 20 g sample, and the resultant mixtures were blended in a steel ball mill for an hour. About 20 g of the mixture was then molded to a 25 mm diameter-17 mm thick pellet by applying a pressure of 50 MPa, followed by pre-reduction.

2.2. Pre-reduction

To minimize the scattering of the sample pellet in the initial heating stage of carbon reduction smelting, pre-reduction was carried out in a vacuum furnace at 1473 K and 1.3 Pa for 2 hrs. The results of X-ray diffraction for products after pre-reduction revealed the presence of only NbC and NbO_2, together with mass losses ranging from 27 to 29%; consequently, the pre-reduction reaction may proceed in accordance with Eq. (2).

$$Nb_2O_5 + 5C = 4/3NbC + 2/3NbO_2 + 11/3CO \qquad (2)$$

The products of pre-reduction were finely crushed and molded to 14 g pellets (20mm diameter x 14mm thick) by a pressure of 50 MPa, and subjected to carbon reduction smelting.

2.3. Carbon Reduction Smelting with Ar Plasma Arc Heating

Figure 2 shows the plasma torch and reaction vessel of the plasma arc furnace schematically. The plasma torch is the transfer-type of d.c. arc discharge, and its maximum power is 20 kW. A pre-reduced pellet was first placed on the water-cooled copper crucible, the reaction vessel was closed and filled with Ar gas after evacuation by a rotary pump, and finally the pellet was subjected to carbon reduction smelting by means of Ar plasma arc heating. The distance between the torch end and the sample was about 2 cm. High-purity Ar gas (>99.9995%) was used as the plasma gas, its flow rate being 5 l/min, and the pressure in the furnace was atmospheric at time of reduction. Since carbon reduction smelting was carried out at about 2,900 K, the arc voltage and current were 35 V and 150 A, respectively.

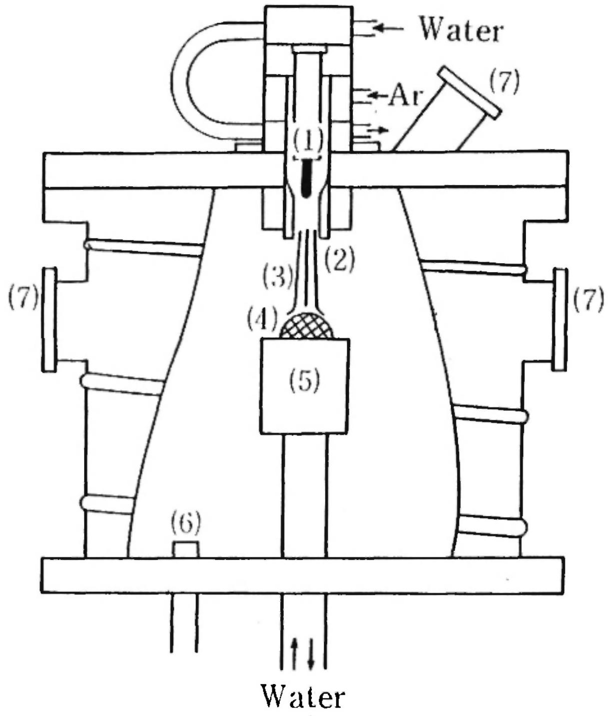

Fig. 2: Schematic diagram of plasma arc furnace.
(1) cathode, (2) anode (copper nozzle), (3) plasma arc, (4) heated sample, (5) copper crucible, (6) gas outlet, (7) viewing port,

With regard to the temperature of heated samples during reduction, refractory metals such as W, Re, Ta, Mo, Nb, Hf and V were heated as standard samples, /12/, and the relation between outputs of Ar plasma arc and each melting-down temperature of heated metals was obtained as shown in Fig. 3, followed by determination of the output required for reaching a given temperature on the basis of the calibration curve shown therein.

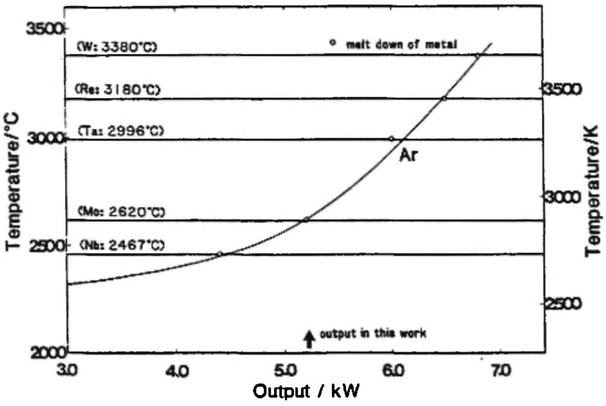

Fig. 3: Relation between the temperature of heated materials and output of Ar plasma arc: calibrated by melting point of several refractory metals.

Argon plasma arc heating enabled the pre-reduced pellet to be completely melted to a button state in about 90 sec. In a series of experiments, the reaction time when the button state is attained was set as zero, and carbon reduction smelting was applied for 12 min with the button turned over 4 times at intervals of 3 min.

2.4. *Electron Beam Melting*

Figure 4 shows the electron beam furnace; its maximum power is 7.5 kW (accelerating voltage: 10kV, beam current: 750 mA). A reduced niobium was placed on the water-cooled copper hearth, and melted for 10 min at 4 kW (10 kV, 400 mA). The melted button was turned over and melted again for 10 min under the same conditions, total melting time being 20 min. Although the degree of vacuum in the furnace before melting was about 2.7×10^{-3} Pa, it rose to 7.0×10^{-3} Pa in the initial stage of melting, and then decreased gradually to $1.3 \sim 2.7 \times 10^{-3}$ Pa.

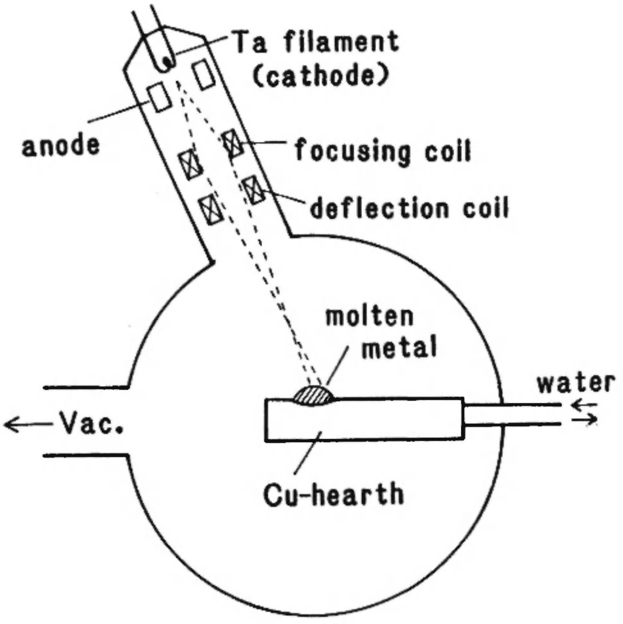

Fig. 4: Schematic diagram of the electron beam furnace.

Niobium products obtained at each stage were analysed by the following methods: carbon was analysed by oxygen gas combustion-coulometric titration, oxygen, nitrogen and hydrogen by inert gas carrier-infrared spectroscopic analysis, and metal impurities by flameless atomic absorption analysis or by ICP atomic emission spectrometry.

3. RESULTS AND DISCUSSIONS

3.1. *Carbon Reduction Smelting with Ar Plasma Arc Heating*

3.1.1. *Effect of Reduction Reaction Time*

Figure 5 shows the change in oxygen, carbon contents and the amount of niobium calculated roughly from the equation Nb (%) = 100-C(%)-O(%) at various C/Nb_2O_5 ratios with the reaction time. The values at time zero indicate analysis when the pellet was melted down to the button state, which already contains above 95% Nb. This result suggests that the pre-reduced pellet was reduced rapidly in about 90 sec. Reaction at this stage is the solid-liquid reduction reaction between carbon or niobium carbide and niobium oxides.

The results shown in Fig. 5 give the progress in reduction after melting; in other words, the progress in deoxidation and decarburization due to the mutual reaction between carbon and oxygen in the Nb-C-O melt as represented by Eq. (3). The oxygen and carbon contents decrease slowly

$$\text{C (in liq.Nb)} + \text{O (in liq.Nb)} = \text{CO (gas)} \qquad (3)$$

at a C/O mole ratio of about one, up to 6 min, and deoxidation and decarburization rates become extremely slow after 9 min. When the C/Nb_2O_5 ratio was 4.9 and 5.0, 12 min-reaction time resulted in niobium with purity of above 99.6%. Further reaction time may reduce the carbon and oxygen content. However, taking into account the purification effect of the subse-

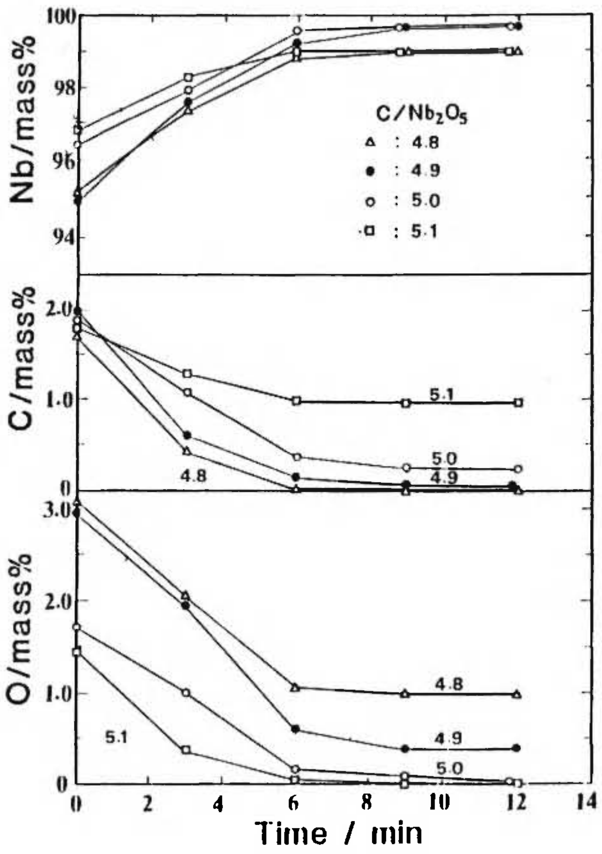

Fig. 5: Effect of reaction time on C, O and Nb contents of the Nb products obtained by carbon reduction smelting.

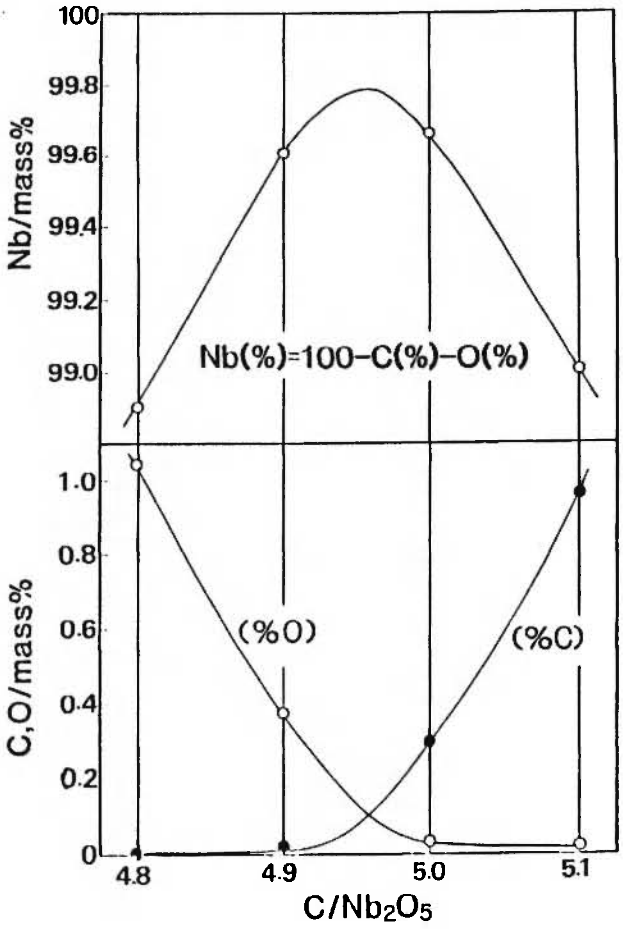

Fig. 6: Effect of C/Nb_2O_5 ratios on C,O and Nb contents in the reduced Nb at 12 min.

quent electron beam melting, long term carbon reduction smelting is not efficient, and 12 min smelting is therefore recommended.

3.1.2. *Effect of Carbon Mixing Mole Ratio on Nb_2O_5 (C/Nb_2O_5)*

Figure 6 shows the effect of C/Nb_2O_5 ratio on carbon, oxygen and niobium contents of 12 min-reduced niobium. As predicted, the carbon content increases and, conversely, the oxygen content decreases with the increasing C/Nb_2O_5 ratio. As a result, it is possible to produce niobium with above 99.6% purity at 4.9 to 5.0 of C/Nb_2O_5. Thus, the carbon and oxygen remaining in reduced niobium depend largely on the C/Nb_2O_5 ratio. Selection of a suitable C/Nb_2O_5 ratio enables adjustment of the carbon and oxygen contents of reduced niobium, taking into consideration the refining effect of the subsequent stage.

In the present work, electron beam melting follows carbon reduction smelting, in which marked deoxidation can be expected; accordingly, reduced-niobium ($O > 0.3\%$, $C < 0.02\%$) produced at 4.8 to 4.9 of C/Nb_2O_5 is preferable as the feed material to electron beam melting.

Photograph 1 shows niobium products obtained by 12 min-carbon reduction smelting at various C/Nb_2O_5 ratios. Niobium obtained at 5.0 of C/Nb_2O_5 shows

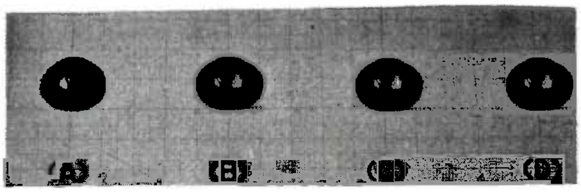

Photo. 1 Nb products obtained by 12 min-carbon reduction smelting, (A) $C/Nb_2O_5 = 4.8$, (B) $C/Nb_2O_5 = 4.9$, (C) $C/Nb_2O_5 = 5.0$, (D) $C/nb_2O_5 = 5.1$,

metallic luster, which turns into a dull silver color with increasing oxygen content (in the case of 4.9 to 4.8 of C/Nb_2O_5).

3.1.3. Relation Between Residual Oxygen and Carbon

Figure 7 gives the relation between carbon and oxygen contents in the 12 min reduced-niobiums, suggesting that the products of their concentrations are nearly equal, as shown in Eq. (4), and that the C-O curve is hyperbolic.

$$(\%\ C) \times (\%\ O) \approx 9.53 \times 10^{-3} \qquad (4)$$

The curves (A) and (B) in Fig. 7 show the relation between carbon and oxygen in carbon reduced-niobium in vacuum, as reported by Ono et al /5/. In their experiments, carbon reduction of Nb_2O_5 under continuous evacuation proceeded during 1.5 hrs of increasing temperature from room temperature to 2,073~2,173 K, followed by vacuum degassing in solid phase under conditions (A) for 3 hrs at2,073 K and 0.13 Pa, (B) for 1 hr at 2,273 K and 0.13 Pa. The results of the present work are closer to the curve (B), indicating that the reduction in the liquid phase proceeds rapidly as compared with the solid phase. Thus the use of plasma arc as the heat source shortens the reduction time and produces niobium efficiently, though it requires a large amount of energy over a short period.

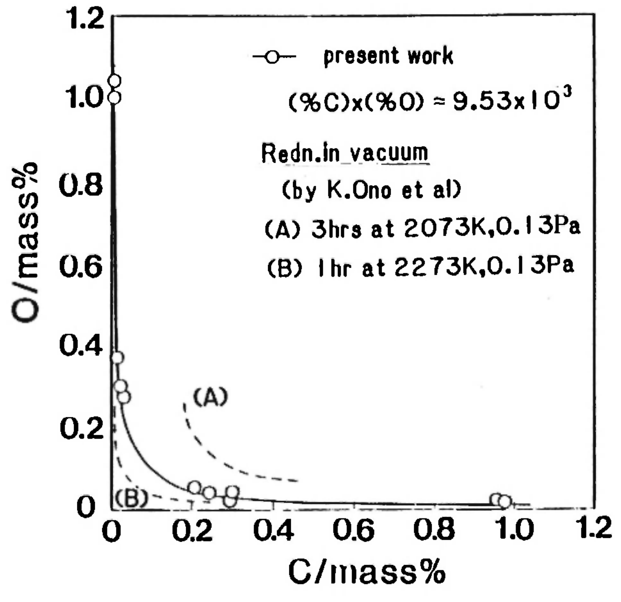

Fig. 7: Relation between carbon and oxygen contents (mass%) in Nb products obtained by carbon reduction smelting of 12 min.

The relation of residual carbon and oxygen was then discussed thermodynamically. No thermodynamic study has been found concerning high-temperature behavior of Nb-C-O melts, but Fromm, et al / 13/. and Ueda, et al. / 14/. reported those of Nb-C-O solid solutions. Equation (5) represents the relation between the equilibrium pressure of CO and the carbon and oxygen contents in the Nb-C-O solid solutions. To evaluate our experimental

$$\log P_{co} = \log (C_c' C_o) + 8.29 - 1.52 \times 10^4/T \qquad (5)$$

where P_{co}: equilibrium pressure of CO (Pa) C_c, C_o: carbon and oxygen content in (at %) in Nb

results concretely, extrapolation to2,900K was attempted under the assumption that Eq. (5) is applicable to the Nb-C-O melt. In Fig. 8, carbon and oxygen contents are expressed in at%, converted from mass% of Fig. 7. The curves (a), (b) and (c) in Fig. 8 were calculated from Eq. (5) assuming that the pressures of CO are 4 KPa (30 torr), 1.3 KPa (10 torr) and 0.13 KPa (1 torr), respectively. The C-O curve obtained in the present work lies between the curves (b) and (c), with its concentration product in terms of at% being (at% C) x (at% O) $\approx 3.9 \times 10^{-1}$. When this value is substituted for Eq. (5), equlibrium pressure of CO is 0.44

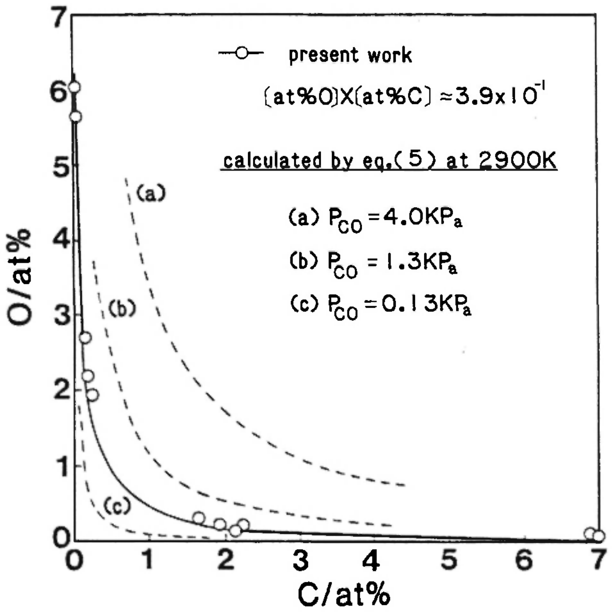

Fig. 8: Relation between carbon and oxygen contents (at%) in Nb products obtained by carbon reduction smelting of 12 min.

KPa (3.3 torr). Although the actual partial pressure around test pieces during reduction smelting is not known, the CO gas produced is always diluted with Ar gas and drawn out of the system; accordingly, the partial pressure of CO is probably smaller than 0.44 KPa. The reduction time of 12 min in this experiment, therefore, seems to be halfway towards equilibrium, and a longer reaction time may reduce carbon and oxygen content further.

3.1.4. Behavior of Metal Impurities

Figure 9 shows the change in iron, silicon and aluminium content in niobium products as the reduction proceeded. The amounts of iron, silicon and aluminium in the newly-melted product (time=0) were 90,51 and 18 ppm, respectively, which were greater than those contained initially in the raw Nb_2O_5 and graphite; i.e. iron and silicon became nearly 3 times as large as those existing in the initial raw material, and aluminium nearly 2.5 times. Iron contamination appears to a rise in the steel ball mill used for blending, whereas aluminium and silicon contamination is due to the crucible materials used for pre-reduction.

During 12 min-carbon reduction smelting, iron, silicon and aluminium decrease to about 60 ppm, less than 3 ppm and less than 10 ppm, respectively. Removal of iron and aluminium may be ascribed to evaporation, while silicon is removed by evaporation of SiO.

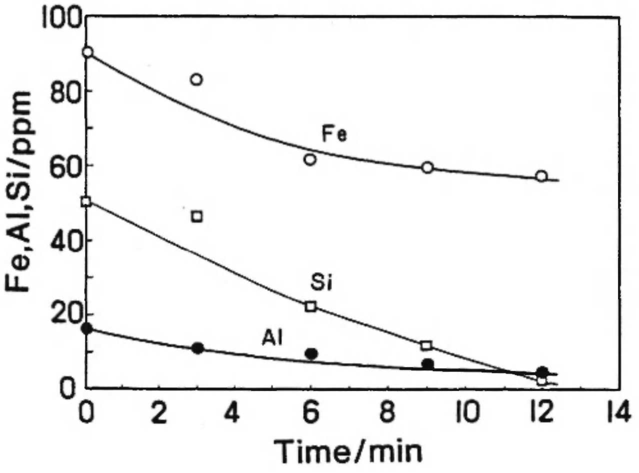

Fig. 9: Changes in Fe, Al and Si contents of Nb products with carbon reduction smelting.

3.2 Electron Beam Melting and Refining

3.2.1. Comparison of Deoxidation and Decarburization Effects.

The niobium products (10.5-11.0 g each) obtained by 12 min-carbon reduction smelting were then subjected to electron beam melting (hereinafter referred to as EBM) of 20 min.

Figure 10 shows the carbon and oxygen contents in niobium and their hardness number in microvickers before and after EBM, as the function of the C/Nb_2O_5 ratio. Figure 10(a), as in Fig. 7, shows oxygen and carbon contents directly after carbon reduction smelting, while Fig. 10 (b) gives those after EBM. Fig. 10(c) gives hardnesses, the broken and solid lines representing the values before and after EBM, respectively.

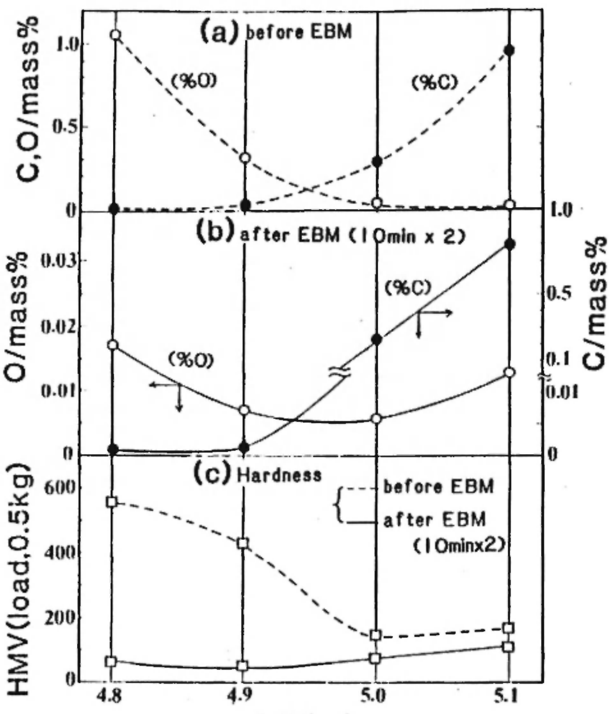

Fig. 10: Change of C, O contents and the hardness of Nb before and after electron beam melting (EBM).
(a) before EBM: same as Fig. 6.
(b) after EBM (10 min x 2, 10kV-40mA).
(c) hardness of microvickers (HMV).

The niobium products obtained with 4.8 and 4.9 of C/Nb_2O_5 ratio contained above 0.3% oxygen and below 0.02% (200 ppm) carbon, but EBM reduced these amounts to about 0.01% (100 ppm) oxygen and under 0.002% (20 ppm) carbon, showing efficient and effective deoxidation and decarburization. Furthermore, as deoxidation by EBM proceeded, the hardness number of niobium products decreased by over 400 to about 50, and ductile niobium metal was produced.

Niobium produced at 5.0 and 5.1 of C/Nb_2O_5 ratio contained below 0.05% oxygen and above 0.3% carbon. Electron beam melting decreased oxygen to about 0.01% (100 ppm), but decarburization proceeded only to a small extent except for CO-degassing, suggesting that carbon cannot be removed without oxygen. These results coincided well with those of Smith, et al. /10/ and Kimura, et al. /11/ obtained from EBM of niobium.

According to the above results, the combination of carbon reduction smelting and EBM enables the production of high-purity niobium (O= 70ppm, C = 20ppm) by reduction smelting at a C/Nb_2O_5 of 4.9 and subsequent EBM.

Photograph 2 shows EBM-treated niobium metals produced from the niobium products given in Photo. 1. Compared with Photo. 1, niobium metal produced from the raw materials obtained at 4.8 and 4.9 of C/Nb_2O_5 ratio were deoxidized to a remarkable extent, showing a clear metallic luster which was silver in Photo. 1; the refining effect is clearly recognized from the external appearance of the resultant niobium metal.

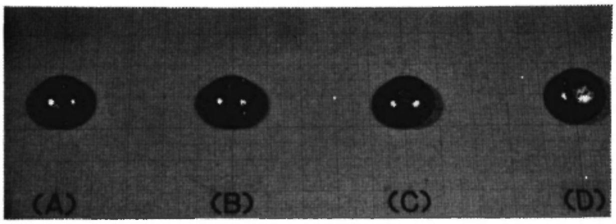

Photo. 2 Nb metals after electron beam melting of Nb products shown in Photo. 1.
(A) C/Nb_2O_5 = 4.8, (B) C/Nb_2O_5 = 4.9,
(C) C/nb_2O_5 = 5.0, (D) C/Nb_2O_5 = 5.1,

3.2.2. Deoxidation and Decarburization Reactions

Figure 11 gives the changes in carbon and oxygen contents in niobium before and after EBM. Concerning the oxygen to carbon ratio, the results obtained in this work can be divided into two cases; (at%O)> (at% C), and (at% O) < (at% C). This classification enables us to understand the difference in the mechanism between deoxidation and decarburization.

1. When the oxygen content is greater than that of carbon before EBM, a marked deoxidation reaction reduces oxygen to a low level, with a small amount of carbon reduced by the CO-degassing reactions as shown by Eq. (3). As reported earlier, it is reasonable to assume that the deoxidation reaction proceeds due to evaporation of NbO and/or NbO_2 /1,10,11/.

2. When the carbon content is greater than that of oxygen before EBM, at least in the initial stage, deoxidation and decarburization proceed to some extent in parallel with the broken line indicating (at% O) = (at% C) in Fig. 11 due to the CO-degassing reaction given by Eq. (3); but decarburization does not proceed further after oxygen decreases to a particular level, which results in excessive amounts of residual carbon in the niobium.

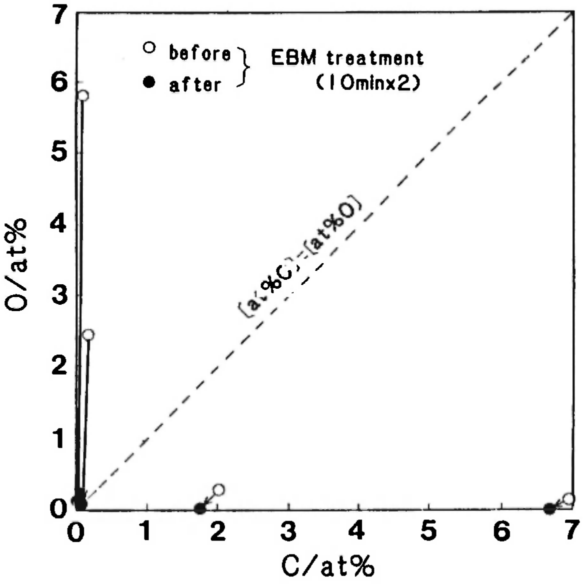

Fig. 11: Changes of oxygen and carbon content in each Nb before and after electron beam melting.

According to Kimura, et al. /11/. the desirable O/C mole ratio in niobium is 3 to 4 in order for deoxidation of EBM to be effective and to minimize residual carbon. In this work, however, high-purity niobium was obtained by applying EBM to higher-oxygen-content niobium products, with an O/C mole ratio of 15 to 20, obtained by carbon reduction smelting at C/Nb_2O_5 of 4.9. It is generally agreed that the deoxidation rate for NbO evaporation is about 4 times as fast as that for CO-degassing /10, 11/, and, in fact, deoxidation proceeded rapidly even at an O/C mole ratio of 10 or more. From these facts, C/O mole ratios of 10 to 20 seem to be effective for reduced-niobium to make the amount of residual carbon as low as possible. However, niobium loss is increased due to evaporation. This will be explained in the succeeding section.

3.2.3. *Niobium Loss Due to EBM*

Deoxidation of niobium due to evaporation of niobium suboxides leads theoretically to niobium-loss, and furthermore, it is considered that the recovery of niobium decreases because of the evaporation of niobium itself. Figure 12 shows niobium recoveries after carbon reduction smelting and after EBM as a function of the C/Nb_2O_5 ratio, with the initial amount of niobium contained in the pellet being the denominator.

Recovery after carbon reduction smelting exceeded 95%. The niobium loss at this point may arise mainly from the scattering of the samples when the pellet reaches the molten state, but adequate pre-reduction treatment appears to decrease scattering to as low as possible.

Recovery after EBM tends to become lower with increased deoxidation. Therefore, in order to estimate the effect of NbO and NbO_2 evaporation on niobium recovery, the following calculations were done for reduced niobium at 4.8 and 4.9 of C/Nb_2O_5 ratio, in which deoxidation was performed by evaporation of NbO or NbO_2. Broken lines (1) and (2) in Fig. 12 correspond to NbO and NbO_2 evaporation, respectively. The actual niobium recoveries were more than 5% lower than the calculated values based on NbO and NbO_2 evaporation, and the difference may be due to evaporation of niobium itself.

The amount of niobium evaporation was then evaluated as to its influence on the decreased niobium recovery. Although the temperature of niobium melted at EBM was not measured for EBM, it is estimated to be about 2,900 to 3,000 K. The vapor pressure of niobium at 2,900 K and 3,000 K was obtained from Eq. (6) /15/,

$$\log P_{Nb}(Pa) = 12{,}128 - 35{,}660/T\ (K) \qquad (6)$$

followed by calculation of the evaporated amount of niobium during 20 min-EBM, by using the Hertz-Langmuir-Knudsen equation. Results indicate that niobium recovery would decrease on account of niobium evaporation by about 2.4% and 5.9% at 2,900K and 3,000K, respectively, suggesting that the decrease of niobium recovery in Fig. 12 would be due to the evaporation of both niobium suboxides and niobium itself.

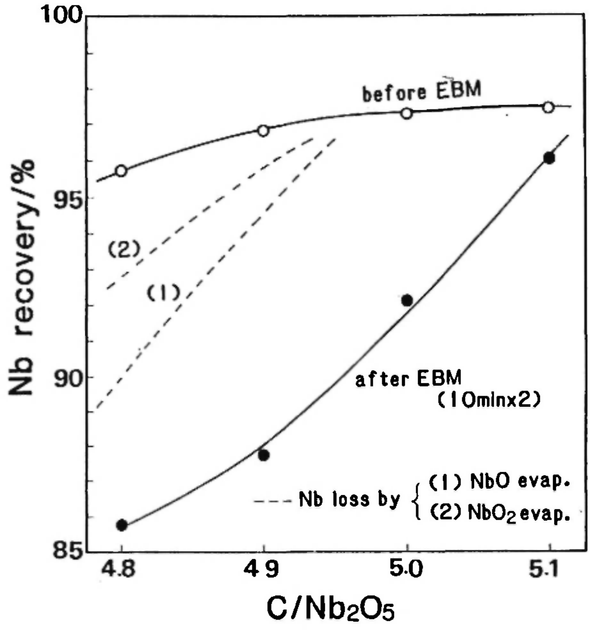

Fig. 12: Recovery on niobium: "before EBM" is the same as that obtained by carbon reduction smelting of 12 min.

To produce high-purity niobium by means of EBM, niobium-loss due to evaporation cannot be avoided, but efforts should be made to shorten the melting time by finding out the shortest time necessary for refining.

3.2.4. *Purification of Niobium by EBM*

Table 2 shows the amounts of impurities in niobium products in each stage, from pre-reduction to EBM, through carbon reduction smelting at 4.9 of C/Nb_2O_5 ratio.

Although the nitrogen and hydrogen contents were 100 to 200 ppm and 10 ppm before EBM, they were reduced to 10 ppm and below 10 ppm after EBM. Schulze, et al. /1/ reported that denitrogenization and dehydrogenation proceed smoothly in accordance with Eq. (7) and Eq. (8), and the results obtained in this experiment coincided well with their views.

$$2\mathit{N}(\text{in liq.Nb}) \rightarrow 2\text{N(on surface)} \rightarrow N_2\ (\text{gas}) \qquad (7)$$

$$2\mathit{H}(\text{in liq.Nb}) \rightarrow 2\text{H(on surface)} \rightarrow H_2\ (\text{gas}) \qquad (8)$$

Metal impurities with a higher vapor pressure than niobium, such as iron, aluminium, and titanium, were readily evaporated and removed by EBM down to 3, 2

TABLE 2: Changes of impurity content in Nb products with each treatment at 4.9 of C/Nb_2O_5 ratio.

Treatment	Element (ppm)												HMV
	Fe	Al	Si	Ta	W	Mo	V	Ti	O	C	N	H	
Pre-reduction	100	19	50	70	20	<1	<1	27					
Carbon redn. (12 min)	58	7	<3	89	15	<1	<1	45	3800	180	170	10	432
EBM (20 min)	3	2	<3	90	40	<1	<1	8	70	20	10	<10	51

and 8 ppm, respectively. On the other hand, removal of tantalum impurity by evaporation was impossible, because of its lower vapor pressure than that of niobium. A tungsten metal impurity unexpectedly increased by 3 times compared with the amount before EBM, although tantalum-filaments were used for the electron beam gun, and the reason for this increase is not yet known.

4. CONCLUSIONS

Fundamental research was carried out on fast reduction of niobium oxides and production of high-purity niobium by a two stage treatment in which carbon reduction smelting by Ar plasma arc heating and electron beam melting were combined.

1. Carbon Reduction Smelting

(1) The pellets with the C/Nb_2O_5 ratios of 4.8, 4.9, 5.0 and 5.1 were carbon-reduction smelted after pre-reduction. The solid-liquid reduction reaction, during which the pellet was heated to the molten state, enhanced reduction rapidly, and the CO-degassing occurring in the Nb-C-O melt allowed over 99% Nb to be produced after 12 min.

(2) The oxygen to carbon ratio in the reduced-Nb depends greatly on C/Nb_2O_5 ratios, suggesting that the O/C ratio in Nb products can be adjusted by selecting a given C/Nb_2O_5 ratio, taking into account the subsequent refining.

(3) The relation $(\%C) \times (\%O) \approx 9.53 \times 10^{-3}$ held true between the oxygen and carbon contents in 12 min-carbon reductions melted-Nb.

2. Electron Beam Melting

(1) Remarkable deoxidation due to NbO and/or NbO_2 evaporation was observed. Carbon, on the other hand, could be removed by CO-degassing only with coexisting oxygen, but excess carbon was barely removed.

(2) The reduced-Nb product (Nb > 99%, C/O mole ratio; 15 to 20) at 4.9 of C/Nb_2O_5 ratio was electron beam melted to produce ductile high-purity Nb (Nb > 99.9%, O=70 ppm, C=20 ppm) with hardness of about 50 HMV.

(3) Nb itself evaporates to some extent as do niobium suboxides resulting in the loss of Nb.

(4) Metal impurities such as Fe, Al, Si and Ti were readily evaporated and reduced to several ppm level.

REFERENCES

1. SCHULZE, K., BACH, O., LUPTON, D. and SCHREIBER, F., *Niobium, ed.* by STUART, H., The Metallurgical Society of AIME., p. 163 (1981).
2. INOUYE, H., *ibid.*, p. 615 (1981).
3. KADO, S., J. Mining and Metallurgical Institute of Jap. (Nippon Kogyo Kaishi), **100**: 142 (1984).
4. DARLING, A. S., Metallurgia, **64**: 7 (1961).
5. ONO, K., UEDA, Y. and MORIYAMA, J., *J. Jap. Inst. Metals* (Nippon Kinzoku Gakkaishi), **43**: 715 (1979).
6. KIMURA, K. and SASAKI, Y., *ibid.*, **26**: 695 (1962).
7. AKASHI, K. and ISHIZUKA, R., J. Mining and Metallurgical Institute of Jap. (Nippon Kogyo Kaishi), **88**: 885 (1972).
8. MIMURA, K. and TANIUCHI, K., *ibid.*, **96**: 165 (1980).
9. MIMURA, K., Soc. of Chemical Engineers, Jap. (Kagaku kogaku), **47**: 437 (1983).
10. SMITH, H. R., HUNT, C. and HANKS, C.W., *J. Metals*, **11**: 112 (1959).
11. KIMURA, K., SASAKI, Y. and UEHARA, S., *J. Jap. Inst. Metals* (Nippon Kinzoku Gakkaishi), **29**: 924 (1965).
12. KUBASCHEWSKI, O. and ALCOCK, C.B., *Metallurgical Thermochemistry*, 5th ed., Pergamon Press (1979).
13. FROMM, E. and SPAETH, G., *Z. Metallkunde*, **59**: 65 (1968).
14. UEDA, Y., ONO, K. and MORIYAMA, J., *J. Jap. Inst. Metals* (Nippon Kinzoku Gakkaishi), **44**: 1069 (1980).
15. BARIN, I. and KNACKE, O., *Thermochemical Properties of Inorganic Substances*, Springer Verlag, Berlin, p. 552 (1973).

(Received September 24, 1987)