Fundamental Study on the Production of Niobium by the Carbothermic Reduction-Electron Beam Melting Combination Method*

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Niobium and niobium alloys have received considerable attention as engineering materials for heat engine applications. In the past several years, the carbothermic reduction-electron beam melting combination method has made it possible to prepare pure niobium metal. In this work, the possibilities and conditions for winning the pure niobium by this process have been examined with regard to the following items: (1) Working conditions and analytical results on the Nb-C-O solid solutions obtained by the carbothermic reduction of Nb_2O_5 in vacuum. (2) Vacuum degassing in the solid state. (3) Refining of niobium by electron beam melting. (4) Evaporation deoxidation in the form of niobium suboxides.

The mechanism of refining of the niobium metal by the present method can be characterized by the next steps, carbon is removed by degassing as CO and the elimination of oxygen takes place in the form of CO and volatile suboxides such as NbO and NbO_2. Both phenomena seem to occur during the refining period in the solid state under the vacuum at 2200 K and the subsequent electron beam melting. Accordingly, the carbon elimination is possible only when an excess of oxygen is present at the beginning of electron beam melting. On the other hand, even after the decrease of carbon, the remaining oxygen can be removed by the suboxide evaporation.

With this process the high purity niobium in which both carbon and oxygen contents are reduced to a sufficient degree is obtainable by favorable conditions of reduction and melting.

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†T. Introduction

Niobium has received considerable attention as engineering materials for use in heat engine applications. Darling(1) showed in 1961 that the carbothermic reduction of niobium pentoxide in vacuum is possible. In 1959 Smith(2) demonstrated that electron-bombardment melting is more useful for purification of niobium than the arc-melting of consumable electrode. The combination of carbothermic reduction in vacuum and the electron-beam melting has since been regarded as a feasible process of niobium production for constructive materials.

The most significant part of this process is a combination of vacuum degassing in the solid state at about 2200 K and degassing from the melt surface during the subsequent electron-beam melting. The decarburization via CO and the deoxidation by volatilization of base-metal suboxides make it possible to reduce the carbon and oxygen contents to the order of less than 100 ppm and produce high-purity niobium ingot.

In the present investigation, the possibilities and conditions for the carbothermic reduction of niobium in vacuum and electron-beam melting have been studied with regard to the following points: (1) Relationship between pressure, temperature and concentration of carbon and oxygen in the Nb–C–O solid solutions to obtain the optimum conditions for the required purity metal. (2) Vacuum degassing in the solid state. (3) Electron-beam refining.

II. Outline of the Process

The thermochemical conditions for the carbothermic reduction of niobium from niobium pentoxide in vacuum may be expected on the basis of the Pourbaix-Ellingham diagram as shown in Fig. 1. For $p_{CO}=10^3$Pa, the temperature range at which the niobium metal phase is stable is higher than the niobium melting point of 2700 K. This may be technologically by an infeasible reduction condition

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because of lack of supporting materials suitable for niobium melting.

The range of the existence of niobium metal is extended by a lowering of the pressure. At the pressure of 0.1 Pa the limiting temperature is 1700 K and at higher temperatures the equilibrium compositions of carbon and oxygen in the Nb metal phase are brought to a further pure metal field.

In this process, the niobium pentoxide is reduced with carbon to lower oxide and carbide during the first reduction period and then refined to homogeneous Nb–C–O solid solutions in the following refining stage. The subsequent melting in an electron-beam furnace lowers the carbon and oxygen contents and transforms the sintered metals into ingot. A complete homogeneity and excellent control of the residual interstitial element contents in the niobium are essential for making this manufacturing process feasible.

### III. Apparatus

The vacuum furnace of 15 kVA at 2300 K with graphite heating element was employed for the reduction of Nb (Fig. 2). The temperature was controlled by means of a SCR-gate controlling system using the e.m.f. of the W-WRe<sub>26</sub> thermocouple. The temperature of specimens was measured with a two color, optical pyrometer.

The vacuum degassing experiments were carried out by using the high temperature vacuum furnace of 10 kVA at 2500 K with a tantalum heating element as shown in Fig. 3. The temperature of samples was measured by the W-WRe<sub>26</sub> thermocouple. The stability of temperature was ±5° at 2500 K.

The electron-beam furnace used for the melting of Nb consists of two guns rated at 40 kW and a water-cooled copper crucible.

The fusion extraction apparatus was used for the oxygen determination in Nb by the carrier gas-coulometric titration. The same apparatus was also fitted to the carbon analysis by the
Powdered Nb$_2$O$_5$ of 99.9% purity was mixed with the graphite powder of 99.6% purity in Nb$_2$O$_5$ to C mole ratio of 1:5 according to the stoichiometric reaction (1),

$$\text{Nb}_2\text{O}_5 + 5\text{C} = 2\text{Nb} + 5\text{CO}, \quad (1)$$

and this mixture was cold-pressed in the form of a square bar of 10×10×50 mm under a pressure of 49 MPa.

The reduction was carried out in a graphite crucible under continuous evacuation. The changes of pressure and temperature in the furnace is shown in Fig. 4. The noticeable evolution of gas occurred at about 1400 K, and after the evolution of gas almost ceased, the sample was subsequently refined at the pressure of less than 1 Pa and at around 2273 K for several hours. When the reduction was completed, the sample was quenched into the cold zone of the furnace. The final products did not adhere to the graphite crucible and exhibited a porous and sponge-like state.

The reduction process may be divided in two periods, the main reduction period at which the reduction of oxide proceeds with the evolution of CO gas and the refining period at which the reduction is almost completed and only the decomposition of the residual suboxide and subcarbide occurs. In this work, the instant when the furnace pressure reaches 1 Pa is considered to be the starting time of the refining period.

Figure 5 represents the relationship between carbon and oxygen contents in the niobium obtained by the carbothermic reduction in vacuum with various conditions of reduction.
metals obtained by the carbothermic reduction of Nb$_2$O$_5$ with various conditions of the Nb$_2$O$_5$ to C mixing ratio, the temperature and the duration of refining period. It can be seen from Fig. 5 that the amounts of carbon and oxygen decreased with increasing temperature and reaction time, and that they are in inversely proportional relation at constant temperature and duration.

The equilibrium thermochemical data on the Nb–C–O solid solutions may be useful for considering the possibilities of purification, although equilibrium is in practice unattainable even under ultimate CO-pressure because the process with continuous evacuation is dynamic and irreversible. Fromm et al.(3) have determined the relationship between equilibrium CO-pressure, temperature and composition of the Nb–C–O solid solutions at 2073–2473 K. Since the C and O compositions represented in Fig. 5 are much higher than the C and O compositions to be obtainable under equilibrium conditions of the same temperature and CO-pressure, it may be possible by a prolongation of refining time to reduce the C and O contents to a degree approaching the equilibrium levels.

It has been recognized from the above reduction experiments that the residual C to O ratios in the reduction product reduced niobium greatly depend on the C to O atomic ratio in the starting materials. Then the reductions of Nb$_2$O$_5$ by carbon of various mixing ratios were carried out, and the C to O atomic ratios in the starting materials were plotted against the C to O atomic ratios in the produced metal in Fig. 6. It is seen from Fig. 6 that the increase in the C to O atomic ratio of the starting material results in the noticeable increase in the C to O atomic ratio of the reduced metal. The Nb–C–O solid solution equilibrates with Nb$_2$C and NbO. Therefore, the carbide and oxide formation will occur in the reduced niobium according to an excess or a shortage of carbon in the starting material respectively.

From the thermodynamic conditions of reduction, the CO degassing is considered to be predominant throughout the reduction. However, as the reduction is, in practice, performed by raising the temperature, the CO$_2$ degassing will also take place during the initial reduction stage when the temperature is relatively low. Moreover, the degassing via NbO and NbO$_2$ has to be taken into account particularly during the final reduction period. From the study of Knudsen cell-mass spectrometry which has been done in parallel, the gaseous molecules of NbO and NbO$_2$ were found over the condensed NbO phase. Nevertheless, the CO degassing is overwhelming during overall reduction process, and the deoxidation via niobium suboxides becomes important at the end of reduction period when the carbon content in the metal is sufficiently decreased.

**V. Vacuum Degassing in Solid State**

The niobium obtained by the carbothermic reduction in the solid state exhibits a porous and sintered form. Because in this reduction process the reduction kinetics largely depends on the rate of degassing of CO, the porous state with a large total surface area from which reacted gas can be evolved would be advan-
tageous compared with the reduction in the liquid state.

The mechanism of refining of the metals by the present method can be characterized by the next steps, that is, carbon is removed by degassing as CO and the elimination of oxygen takes place as CO as well as volatile suboxides such as NbO and NbO₂. The equilibrium vapor pressures of the gaseous components in equilibrium with the Nb–O and Nb–C–O solid solutions are summarized in Fig. 7. The vapor pressure of NbOₓ, which represents the gas mixture of NbO and NbO₂, is much lower than the CO partial pressure. However, when the contents of carbon and oxygen in the niobium are very small at the refining period, the probability that the matrix niobium metal combines with the dissolved oxygen to form the volatile suboxides and this suboxide leaves the surface will be significant rather than the CO gas formation. To find the degassing mechanism, experiments on the solid-state degassing of the Nb–C–O solid solutions have been carried out as follows.

The solid niobium metals containing various amounts of carbon and oxygen were prepared by carbothermic reduction of Nb₂O₅ in vacuum and were cut into small particles of 1 mm in diameter. The sample contained in a tantalum container was suspended with a tungsten wire in the vacuum furnace shown in Fig. 3. After being vacuum-degassed at a given temperature between 2073 and 2473 K and 1.3 x 10⁻² Pa, it was quenched in a water-cooled copper cup at the bottom of the furnace and analyzed for carbon and oxygen. The carbon and oxygen contents before and after the vacuum degassing are plotted in Fig. 8. From these results the following facts may be confirmed. (1) If an excess of carbon is present in the metal before degassing, the carbon and oxygen can be removed by the C/O atomic ratio=1 and the carbon remains after the degassing. (2) On the other hand, if oxygen is present in excess in this case, the degassing proceeds with the smaller than one atomic ratio of C/O and the carbon can be effectively removed at the same time. (3) The oxygen can be eliminated even if the carbon is not present. As a result, it may be predicted that the purification of niobium proceeds by the decarburization forming CO and the deoxidation via suboxides.

By considering the evaporation deoxidation via metal suboxides from thermodynamic point of view, Brewer(8) has demonstrated that the possibility of purifying metals contaminated with oxygen by vacuum distillation may

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**Fig. 7** Equilibrium vapor pressures over the Nb–O and Nb–C–O solid solutions at 2273 K.

**Fig. 8** Correlation of the carbon and oxygen levels in niobium before and after the vacuum degassing in solid state.
be well predicted by the oxygen to metal ratio in the vapor phase compared with the oxygen to metal ratio in the metal phase. The evaporation ratio $R$ was defined as

$$R = \frac{(O/M)_{\text{vapor}}}{(O/M)_{\text{metal}}}.$$  \hspace{1cm} (2)

A favorable purification effect can be only expected if the value of $R$ becomes materially greater than 10. On the contrary, the evaporation loss of metal is important if the value of $R$ is close to 1. The overall O/M atomic ratio in the vapor is defined by

$$\frac{(O/M)_{\text{vapor}}}{(O/M)_{\text{metal}}} \sum \frac{y_{\text{PM}_2\text{O}_y}}{x_{\text{PM}_2\text{O}_y}}$$ \hspace{1cm} (3)

where $p$ is the partial pressure of the gas being considered. Calculation of $R$ for the Nb–O solid solution containing 100 ppm of oxygen gives $R=10^4$ at 2273 K. This implies that the oxygen in Nb can be effectively eliminated by the evaporation of suboxides.

VI. Electron Beam Refining

The niobium metal obtained by carbothermic reduction was melted in the form of a 0.01 kg button by using a 40 kVA electron beam furnace. The melting time was 600 s under a vacuum of $1.3 \times 10^{-2} - 4.0 \times 10^{-3}$ Pa. The carbon and oxygen levels in the niobium before and after melting are represented in Fig. 9. It is seen from Fig. 9 that the oxygen removal is much easier than the carbon elimination as indicated by Kimura et al.\(^{(9)}\) The carbon elimination is possible only when an excess of oxygen is present in the metal before melting. The mechanism of metal suboxide volatilization may be also applied to the estimation of the deoxidizing tendencies in niobium during electron beam melting.

Fig. 9 Correlation of the carbon and oxygen levels in niobium before and after melting in the electron beam furnace for 600 s.

VII. Role of Evaporation Deoxidation

In the production process of niobium consisting of the combination of the carbothermic reduction in vacuum and the electron beam melting, the control of carbon and oxygen contents in niobium ingot is considered to be a major problem. In this work, the conditions for this control have been investigated from the thermodynamic standpoint. The study shows that it is possible to reduce the carbon and oxygen contents in niobium to less than 100 ppm. Although this is essentially due to the very low vapor pressure of niobium, the volatile behavior of niobium suboxides plays an important role.

It has been pointed out that the excess carbon contained in the Nb–C–O solid solution as compared with oxygen remains and is condensed in the metal after the electron beam melting. Therefore, it is, in practice, preferable to produce the niobium containing an excess oxygen by the carbothermic reduction and subsequently eliminate the residual oxygen by volatilization of suboxides in the electron beam furnace. In consequence, it may be said that two unit operations, the carbothermic reduction in vacuum and the electron beam melting, are interdependent to produce the niobium of commercial grade.

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