

Editor's Announcement

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Characteristic Variation of Niobium Powder Produced under Various Reduction Temperature and Amount of Reductant Addition

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This paper has been retracted by the editorial committee with the first author's agreement due to substantial overlap with the following paper previously received in another journal.

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THE MANUFACTURING OF NIOBIUM POWDER BY HUNTER PROCESS

Jae-sik Yoon

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And thus, it shall not be regarded as an original paper.

The first author acknowledges the substantial overlap and his apologies have been accepted accordingly. The notice has been issued to all the authors to pay more careful attention in submitting papers.

Characteristic Variation of Niobium Powder Produced under Various Reduction Temperature and Amount of Reductant Addition

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Niobium powder was fabricated by sodiothermic reduction process using K_2NbF_7 as the raw materials, KCl and KF as the diluents and Na as the reducing agent. The apparatus for the experiment was designed and built specifically for the present study. Varying properties of niobium powder depending on reaction temperature and excess of reducing agent were analyzed. The niobium particle size increased significantly as the reduction temperature increased from 993 to 1093 K. The particle size was fairly uniform at a given reaction temperature, varying from 0.2 μm to 50 nm, depending on the reaction temperature. The yield of niobium powder increased from 58 to 83% with an increasing reaction temperature. The average particle size of niobium powder is improved from 70 nm to 0.2 μm with an increasing amount of sodium excess. And the yield ratio of Nb powder was 82% in the 5% excess of sodium. [doi:10.2320/matertrans.M2009192]

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Keywords: niobium powder, metal-thermic reduction, diluent, reaction temperature, reducing agent, particle size, yield

1. Introduction

Niobium (Nb) has a small neutron absorbing cross-sectional area, outstanding ductility, oxidation resistance and impact-resistance, and high transition temperature (8.2 K), so the metal is used widely in nuclear fusion, nuclear industry, space development, high-power transmission and steel and superconductor. The melting point of niobium is as high as 2,740 K, its density is 8.55 g/cm³ and dielectric dissipation is higher than tantalum. Particularly as niobium is superior in the rectification of oxidized film, which is obtained from the oxidation of anode, and in dielectric dissipation and electric stability, it has all desirable properties as a material of capacitors for electronic appliances and thus is spotlighted as a substitute to tantalum. Niobium and tantalum are rarely found apart in nature and never in the free state. Element niobium amounts to 20 ppm in crustal abundance. In comparison, tantalum is a scarcer metal with abundance only a tenth of niobium. On account of their similar properties and similar atomic and ionic radii, these elements have strong geochemical coherence. Niobium is vital as an alloying element in steels and superalloys for aircraft turbine engines, and is in the greatest demand in industrialized countries.¹⁻³⁾ Niobium powder can be obtained by reducing niobium oxide with magnesium, aluminium, calcium or carbon, or by reducing niobium chloride with hydrogen.⁴⁾ However, the reduction of niobium oxide with metals poses difficulties when it comes to controlling the size and shape of niobium powder particles.^{5,6)} Using carbon poses other difficulties; it requires temperatures higher than 1723 K, and there is a risk of carbon contamination.⁷⁾ The process of hydrogen reduction of niobium chloride has not been commercialized because of the highly hygroscopic property of chloride and the reactivity of the by-product HCl.⁸⁾ The final physicochemical properties of niobium

powder are determined by various factors including the conditions of reduction, vacuum heat treatment and deoxidation treatment after reduction. Though the principle of the Hunter process is well known, very little has been published about the actual details of the process, which has been much improved upon the Hunter's original ideas.⁹⁾ Even the basic technology of the reduction process itself is rigorously protected by companies in technologically advanced countries. Niobium powder was made from potassium heptafluoronio-bate (K_2NbF_7) using sodium (Na) as a reductant, and KCl and KF as diluents based on the Hunter sodiothermic reduction method. Particularly as niobium is superior in the rectification of oxidized film, which is obtained from the oxidation of anode, in dielectric dissipation and in electric stability, it has all desirable properties as a material of capacitors for electronic appliances and thus is spotlighted as a substitute to tantalum. In the present study, the influence of variables such as reduction temperature and the amount of sodium excess in the charge and scale of reduction on the yield and particle size, has been studied.

2. Experiment

The diagram of the experimental apparatus is shown in Fig. 1. The apparatus includes a stainless steel reaction chamber inside an electric furnace, continuous supply equipment of Na, an atmosphere controller, an Ar gas supplier, a cooling zone, and an air exhauster. The reaction chamber can be evacuated to prevent oxygen contamination, and the reactants can be stirred to facilitate the reduction process.

The experimental process can be briefly described as follows. A stainless steel bomb as shown in Fig. 2, (120 mm in diameter, 140 mm in height and 2 mm in thickness) was used as a reduction opened vessel. This vessel was charged with K_2NbF_7 as the raw materials, and slices of sodium, KCl and KF as the diluents in alternate layers. KCl and KF were prepared as diluents salts at a mass ratio between the KCl and

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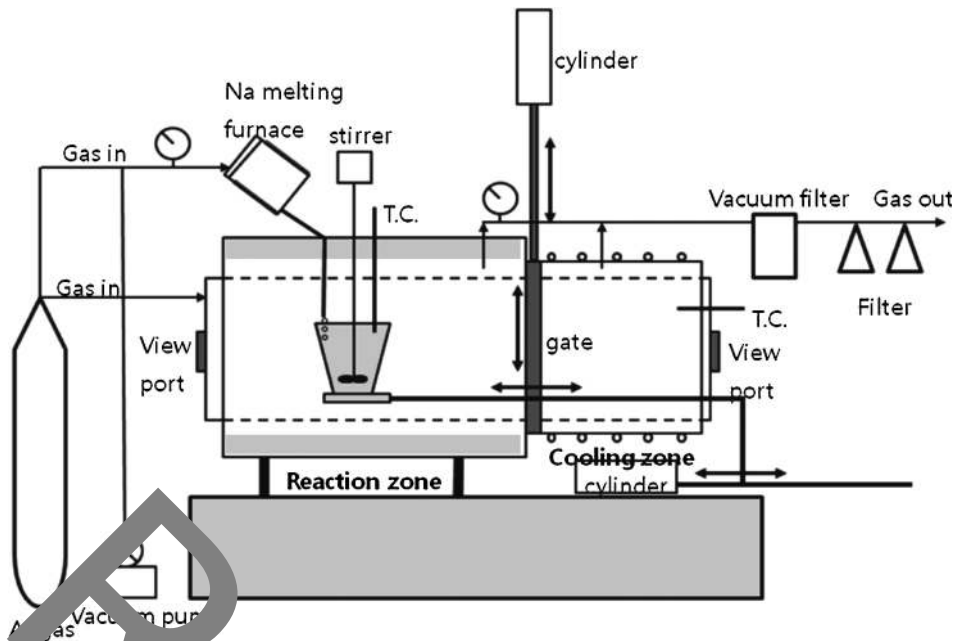


Fig. 1 Schematic diagram of the niobium reduction apparatus used in the study.

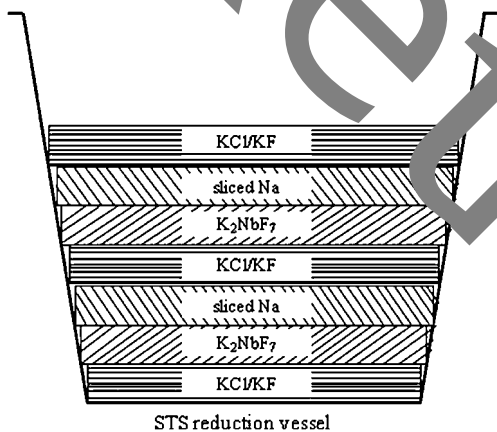


Fig. 2 Filling procedure of raw materials, reductant and diluents into a vessel.

the KF of 1 : 1 and total weight of 100 g, while that between K-salt (K_2NbF_7) and the diluent salts was 1 : 2. In addition, 50 g of K-salts and metallic sodium in fine slices was in the preparation. The diluent salt was placed at the bottom and the top of the charge.

Niobium uses a vacuum chamber because it has strong chemical affinities with oxygen and nitrogen. The vacuum chamber, which was 400 mm in diameter, 700 mm in length, 5 mm in thickness and 3.99 Pa in pressure, was made of stainless steel sheet. A series of operations from exhaustion to Ar gas injection was performed three or more times as an effort to minimize the amount of oxygen inside the reaction chamber. In this study, we also installed a stirrer of Ni-based alloy in the center of the reaction vessel to promote the reactions of the raw materials, diluents, and reducing agents dissolved during the reduction process. Reaction temperature was raised to the target temperatures. In this study, reduction was conducted for 2 h. The stirrer was placed 5 mm above the bottom of the vessel, and stirring was performed a rate

of 50 rpm during the reaction. After the completion of the reaction, the reaction products consisting of niobium and salts were cooled and taken out of the reaction vessel. These products were broken into fragments approximately 5 mm in size, and the salts were washed away with distilled water. After several washings with distilled water, the product was washed and subsequently leached with acid solutions to remove unreacted K-salt and reaction products NaF, KCl and KF. The leaching solution employed were 20% HCl for 1 h and $\{Al_2(SO_4)_3 + H_2SO_4\}$ for 3 h to dissolve fluorides and remove Cr etc. The influence of variables, such as reduction temperature (993 K, 1023 K, 1053 K and 1093 K), and the amount of sodium excess (0%, 2%, 5% and 7% in excess of the stoichiometric amount) in the charge was studied. SEM (Scanning Electron Microscope, Hitachi S-4800), XRD (X-ray diffractometer, Panalytical X'pert pro) and EDS (Energy Dispersive X-ray Spectrometer, Bruker, AXS) studies were carried out to determine the crystal structure, the particle size, shape, and the chemical composition of the powder, respectively.

3. Results and Discussion

To analyze the size and shape of Nb powder particles, SEM photographs were taken. Figures 3 and 4 show scanning electron microscopy (SEM) images of the morphological characteristics of niobium powder manufactured at different reduction temperatures and with different amounts of Na excess. Figure 3 shows that Nb particle sizes increased from 50 nm to 0.2 μm with increase in the reaction temperature. Nb granules grew coarser and larger as the reduction temperature increased from 993 to 1093 K. As granules grew slowly at temperatures below 1023 K, they grew uniformly, forming networks with surrounding granules. A number of large and coarse granules were observed nonetheless. However, it is difficult for the particles to grow because the growth rate depends on the diffusion rate. Conversely, as the reaction

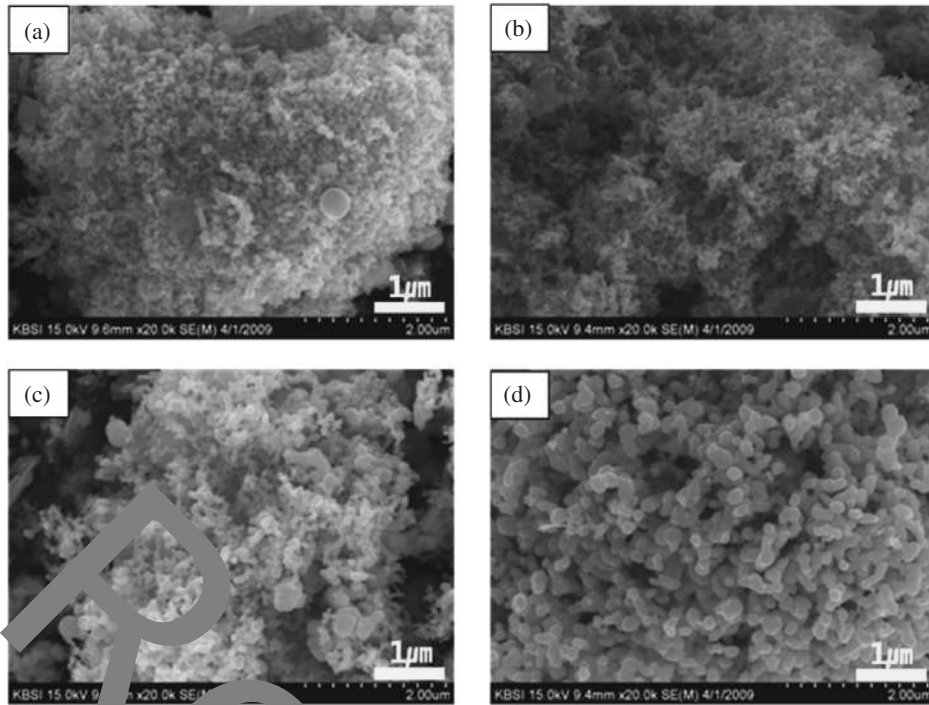


Fig. 3 The dependence of niobium particle size on reaction temperature ($\times 20,000$) (a) 993 K, (b) 1023 K, (c) 1053 K and (d) 1093 K.

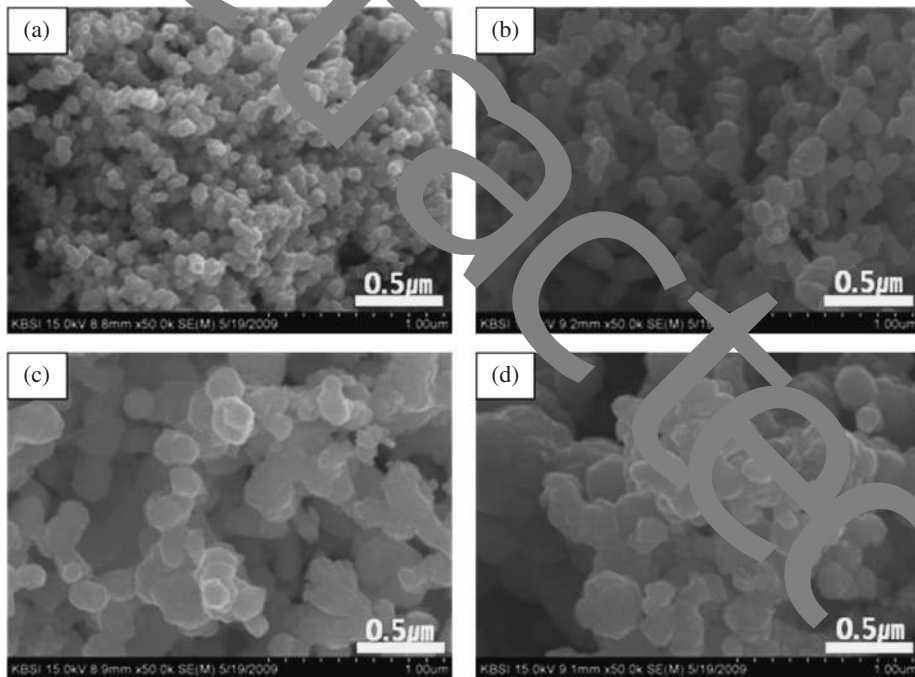


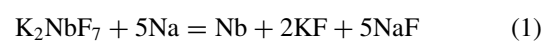
Fig. 4 SEM photographs of niobium particles on amount of sodium excess ($\times 50,000$): (a) 0%, (b) 2%, (c) 5% and (d) 7%.

temperature increases, nucleation becomes more difficult, while growth becomes easier.¹⁰ Figure 3(d) shows the SEM photographs of Nb particles obtained at 1093 K. In general, the particles were relatively uniform and of submicron sizes.

Figure 4 shows that the excess of sodium in the charge increased from 0 to 7% (over the stoichiometric requirement). The percentage of Nb fines (< 50 nm) decreased with increase of sodium excess. Considering the distribution of the particle size on the niobium powder, 5% sodium excess over

the stoichiometric requirement in the charge was found to be optimum for reduction products. In addition, Nb particle size was obtained by $0.2 \mu\text{m}$.

Equation (1) describes the niobium reduction reaction that took place inside the reaction chamber. Because KF, KCl and NaF are all water-soluble, they can be washed away simply with water.



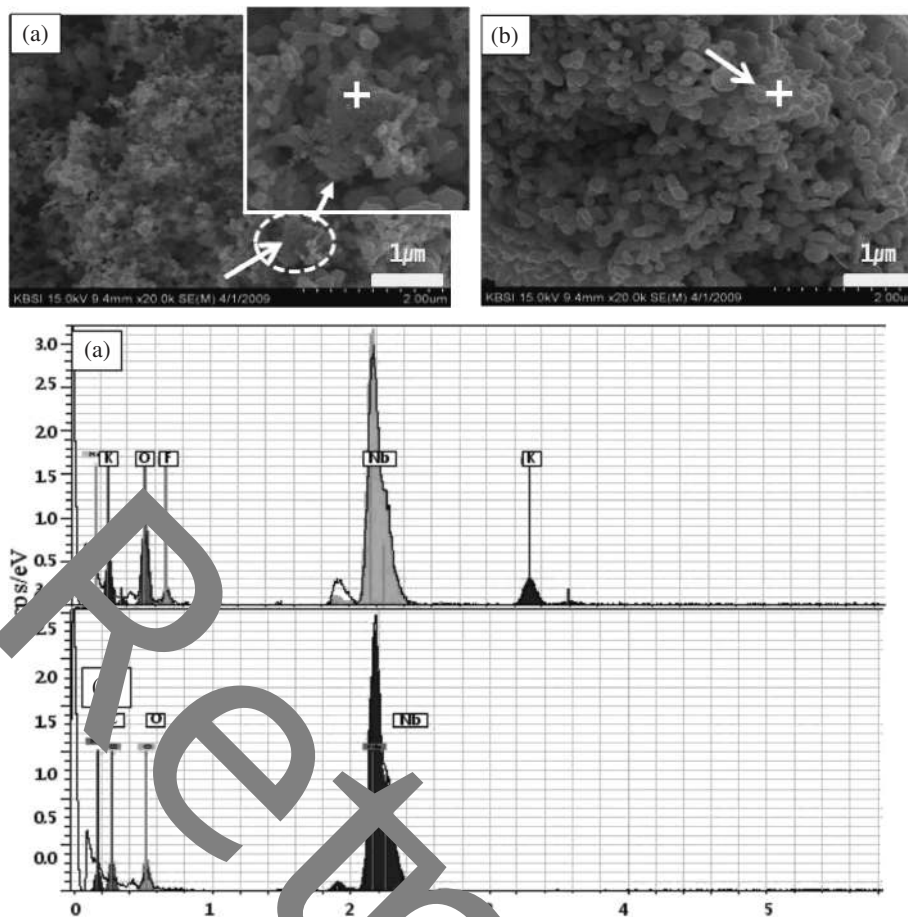


Fig. 5 SEM photographs of niobium particles and EDS point analysis of niobium powder. (a) before acid treatment and (b) acid treatment.

Figure 5 shows the surface of particles and the EDS point analysis of the surface, before (a) and after (b) acid treatment of the product, respectively. As expected, Figure 5(b) shows only the niobium peaks with no evidence of the salts. Figure 5(a) shows miscellaneous peaks other than those of the niobium in the figure, representing the elements picked up in the process of preparing the specimen for the EDS analysis. F and K are from the reaction salts in the charge, and oxygen is considered to have been formed by oxidation due to the low level of vacuum inside the chamber. Therefore, the niobium powder obtained originally in the current experiment can be said to be chemically pure.

The recovery rate of a reduced product can be calculated theoretically using the molecular weight of the raw materials. Given that the Nb content in 1 mol of K_2NbF_7 is 30.6 mass%, theoretically 11.28 g of Nb are produced if 50 g of K_2NbF_7 is reduced 100%. The recovery rate was calculated by vacuum-drying the recovered Nb powder and weighing it using an electronic balance. Figure 6 shows the recovery rate of Nb powder precipitated at reduction temperature ranging from 993 to 1093 K at 5% excess of sodium. As shown in the figure, as reduction temperature increased, the niobium metal recovery rate increased from 58 to 83% at 1093 K. This suggests that the recovery rate increases as the reduction temperature increases.

In addition, the recovery rate was low at reduction temperature most likely because the granule size of precipi-

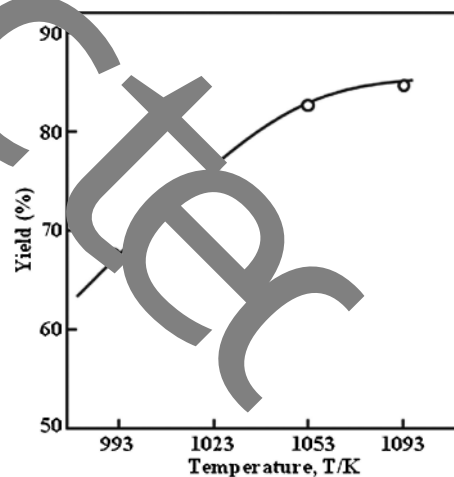


Fig. 6 The influence of the reduction temperature on the Nb powder yield.

tated niobium powder was small. As a result, a large portion was lost by several washings. Figure 7 also shows the recovery rate of Nb powder precipitated at amount of sodium (0%, 2%, 5% and 7% excess of the stoichiometric amount).

The yield of niobium powder improved from 56 to 82% with increase in sodium excess at 1053 K. But the yield of niobium powder decreased at over 7% excess of sodium. In addition, when more than 5% of sodium was used, unreacted sodium deposited on the cooler zone of the reactor and

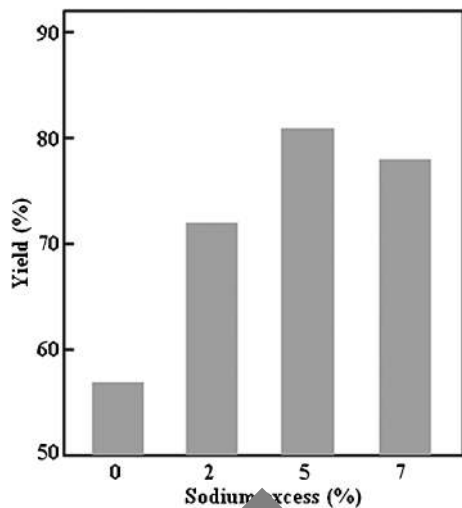


Fig. 7 The influence of the amount of sodium excess on the Nb powder yield.

surface of powder, posed a handling problem in further processing. Considering the yield of Nb powder, 5% excess of sodium over the stoichiometric requirement in the charge was found to be optimum for reduction powder at 1053 K.

4. Conclusions

In order to evaluate the chemical properties of niobium powder manufactured by metallothermic reduction process, the present study concerning the process of making niobium powder was carried out. The following summarizes the results;

- (1) The niobium particle size increased significantly as the reduction temperature increased from 993 to 1093 K. The particle size was fairly uniform at given reaction temperature, varying from 0.2 μm to 50 nm, depending

on the reaction temperature. Nb powder morphology and particle size are very sensitive to reaction temperature in the metallothermic reduction process. The yield of Nb powder increased from 58% to 83% with increasing in reaction temperature.

- (2) Nb powder was obtained by reducing 50 g of K-salt with 5% excess of sodium in the charge at a reduction temperature of 1053 K. The average particle size of niobium powder was improved from 70 nm to 0.2 μm in 5% excess of sodium. The proportion of the fine fraction decreased appreciably and the yield of Nb powder improved from 56% to 82% with the increase in sodium excess.

Acknowledgements

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