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# DIRECT POWDER PREPARATION OF Nb-Ti ALLOY FROM THE OXIDE MIXTURE

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A process to produce niobium-50mass% titanium alloy powder is proposed and its applicability is examined experimentally. The oxide mixture ( $\text{Nb}_2\text{O}_5 + \text{TiO}_2$ ) was exposed to the reductant calcium, which can be applied thermodynamically as either the liquid or the gaseous form. Ca gas was favorable for the contamination of impurity such as carbon. The anhydrated co-precipitation from the aqueous solution involving  $\text{Nb}^{5+}$  and  $\text{Ti}^{4+}$  formed the better uniformity in the obtained alloy powder. The addition of  $\text{CaCl}_2$  reduced the residual oxygen to the level of 0.15mass% because the by-product CaO partially dissolved in the molten  $\text{CaCl}_2$ .

KEYWORDS: NIOBIUM, TITANIUM, CALCIUM CO-REDUCTION, OXIDE MIXTURE, MOLTEN SALT

## I. INTRODUCTION

Nb-50mass%Ti alloy is a valuable superconducting material for practical use, and many attempts have been made to prepare it with the well-concentration control. This superconducting wire is requested to be homogeneous in  $\pm 1.5\text{mass}\%$  Ti and cleaner than 0.1mass% oxygen. Because of the significant difference in vapor pressure, however, it is difficult to mix the alloy elements in the molten state in vacuum. Even arc melted ingots involved a heavy segregation because of the high melting point of Nb, and the Nb-Ti alloy powder could not be obtained suitable for powder metallurgy.

So far the direct compound reduction techniques, called the co-reduction and Reduction-Diffusion (RD) processes, have been successfully used for the preparation of rare earth magnetic materials such as Sm-Co [1], Ti-Al and Nb-Al intermetallic compounds [2-5] and the superconducting  $\text{Nb}_3\text{Sn}$  [6]. The authors reported that the obtained powders were very fine, because they were produced directly from the oxides at low temperatures without melting [2-6].

The chemical reaction to produce Nb-Ti solid solution from oxide mixture can be described by,



Mg or  $\text{CaH}_2$  is also available as the reductant [2-4] because of its stronger affinity with oxygen than Nb and Ti. In case of RD process, Nb or Ti powder is selected as one of the starting materials in eq.(1), but its powder form is hardly obtained. There are also some difficulties in co-reduction depending on: (1) removal of oxygen to the level satisfying the commercial standards, (2) single phase preparation, and (3) concentration control for requested properties [3]. It should be noted that Ti, Nb and Ca are mutually insoluble and that the residual oxygen in Ti and

Nb are 480 mass ppm and 1 ppm level, respectively, when they react independently with Ca [7,8]. Thermodynamically Mg can not remove oxygen in Ti as much as Ca.

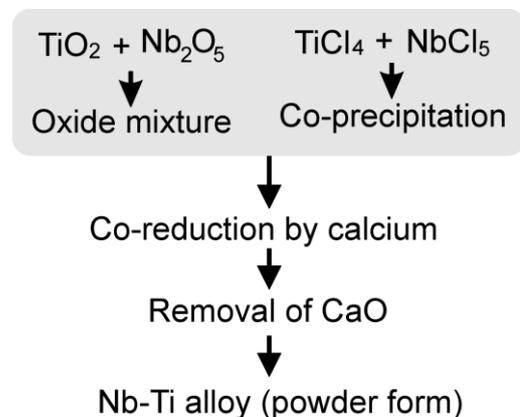
This paper report the results of experimental investigations directed towards the production of clean Nb-Ti alloy powder by Ca co-reduction process.

## II. EXPERIMENTAL PROCEDURE

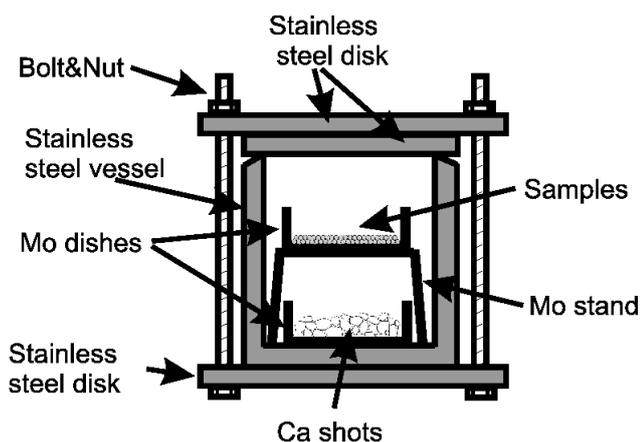
Nb and Ti form the complete bcc solid solution above 1155K. The concentration of the obtained powder will be regulated by the starting concentration in eq. (1).

**Fig. 1** shows the procedure of this work; raw material blending, high temperature reaction and acid leaching for removal of the by-product CaO.

For preparing the oxide mixture, two methods were employed: (1) co-precipitation from chloride solution and (2) mechanical mixing. For the former, high purity  $\text{TiCl}_4$  and  $\text{NbCl}_5$  were dissolved in water and conc. HCl solution, respectively, and they were mixed at a desired atomic



**Fig. 1:** Concepts of Nb-Ti production by Ca co-reduction.



**Fig. 2:** Reaction vessel for co-reduction experiments.

ratio. This solution was dropped into 0.1N  $(\text{NH}_4)_2\text{CO}_3$  aqueous solution and subsequently neutralized by  $\text{NH}_4\text{OH}$ . After separation of the precipitation from the solution,  $\text{NH}_4\text{Cl}$  adhering to it was removed by rinsing several times with distilled water. The white-colored cake was calcined at 1223K for 14.4ks in open air to evaporate any  $\text{NH}_4\text{Cl}$  completely. For (2),  $\text{Nb}_2\text{O}_5$  and rutile ( $\text{TiO}_2$ ) powder were mixed in a desired ratio using agate mortar. The particle sizes were in the order of sub-microns.

The reduction experiments were carried out at 1273K in a stainless steel vessel as shown in **Fig. 2**. In the case of reduction by Ca saturated vapor, Ca was put on the bottom of the vessel, and the oxide mixture was placed on a Mo tray. After heating the sealed vessel in Ar atmosphere, it was cooled in the furnace. The melting point of Ca is 1116K, and its equilibrium vapor pressure is 1750Pa at 1273K. Considering the leakage of Ca from the vessel, the Ca charge was 6-10 times greater than the stoichiometric amount. For the reduction by liquid Ca, Ca granules were mixed with oxide mixture and loaded on the Mo tray.

The reduction products containing the desired alloy powder, the residual Ca and CaO often formed a hard cake especially when liquid Ca was used. They were slurried in  $\text{CH}_3\text{COOH}$  aqueous solution with supersonic vibration or stirring. The centrifugated powder was rinsed with water, alcohol and acetone, then dried in a vacuum.

### III. RESULTS AND DISCUSSION

The powders obtained were identified by XRD analysis and listed in **Table 1**. When the reaction time was shorter,  $\text{CaTiO}_3$  was observed. It shows that  $\text{Nb}_2\text{O}_5$  was preferentially reduced by Ca, and that the by-product CaO reacted with the residual  $\text{TiO}_2$ . Thermodynamically  $\text{CaTiO}_3$  can be reduced to Ti by the additional supply of Ca. When the liquid Ca was applied, XRD peaks for bcc structure were broad or split, reflecting that the lattice parameters of Nb and  $\beta$ -Ti are very close. It indicates a large compositional scatter in the particles.

The oxygen, nitrogen, carbon and calcium in the powder were analyzed chemically, and shown in **Fig. 3**.

The oxygen content decreased as reaction time increased. The reducing rate for the co-precipitated oxides was faster than that for the oxides mechanical mixture. The oxygen content seems to saturate in 0.8-1.0mass%.

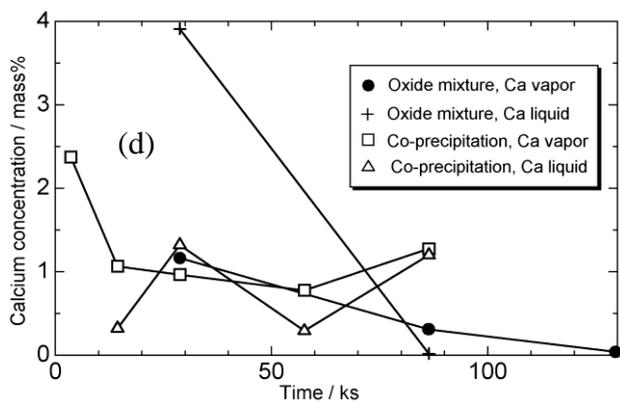
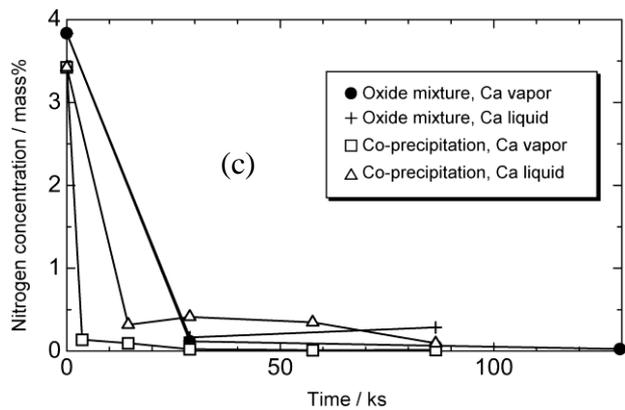
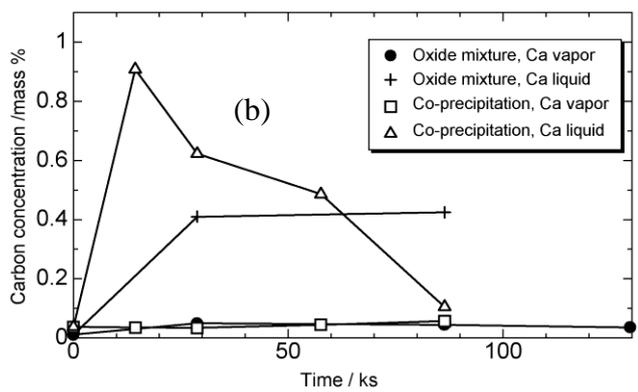
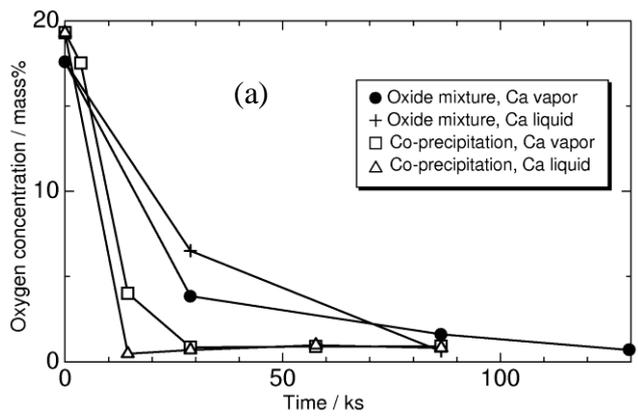
The carbon content increased when liquid Ca was used. Because the main impurities in the reductant Ca are oxygen and carbon, and because the thermodynamic affinities with carbon and nitrogen are greater in Nb and Ti than in Ca [7,8], carbon and nitrogen can be transferred to Nb-Ti powder. When the gaseous Ca attacked the oxide mixture, carbon in Ca did not contaminate the product. Experimentally the increment of carbon content was also affected by the imperfect removal of CaO, because the residual CaO absorbs  $\text{CO}_2$  in the atmosphere. The nitrogen content decreased to be less than 0.02%N in gaseous Ca, while it remained in 0.1%N level when liquid Ca was used. This work used the commercial grade of Ca. It should have been distilled before usage to remove carbon and nitrogen. Ca content in the samples scattered in range of 1%Ca. Because  $\text{CaTiO}_3$  is not dissolved in  $\text{CH}_3\text{COOH}$  solution, the analytical value became larger when the sample contained  $\text{CaTiO}_3$ .

SEM images of the powder are shown in **Fig.4**. The particle size was distributed in the range of 1 to 5  $\mu\text{m}$  when liquid Ca was used. The particles sintered each other and grew to 10-20 $\mu\text{m}$  in size when Ca vapor was used. The particle size depended on the reaction time.

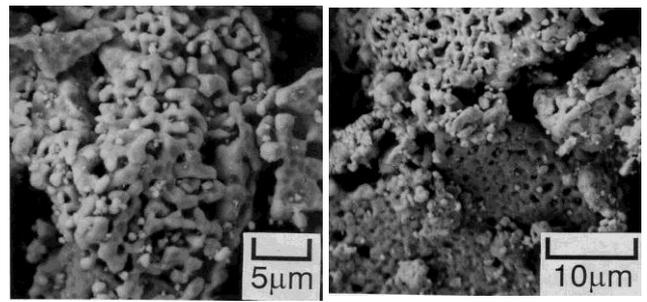
Ti and Nb contents in 5-10 particles were analyzed by EDX, and the relationship between the lattice constant measured by XRD and the concentration analyzed by EDX was shown in **Fig. 5**. The scatter of concentration in

**Table 1:** Experimental conditions and identified phases.

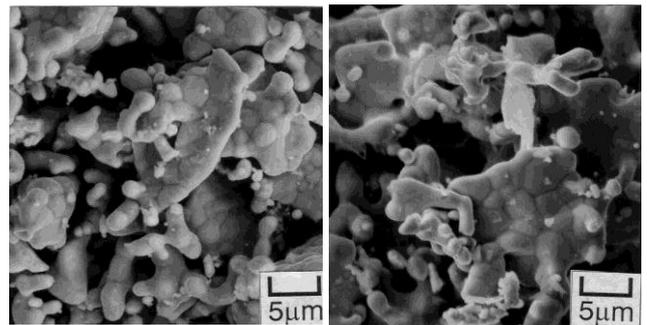
Starting materials	Reductant	Time (ks)	Identified phases by XRD
Mechanically mixed oxide	Ca vapor	28.8	Bcc alloy, $\text{CaTiO}_3$
		86.4	Bcc alloy
		129.6	Bcc alloy
Mechanically mixed oxide	Ca liquid	28.8	Broad peaks, $\text{CaTiO}_3$
		86.4	Split peaks of Bcc
Co-precipitated oxide mixture	Ca vapor	3.6	Broad peaks, $\text{CaTiO}_3$
		14.4	Bcc alloy
		28.8	Bcc alloy
		57.6	Bcc alloy
		86.4	Bcc alloy
Co-precipitated oxide mixture	Ca liquid	14.4	Split peaks of Bcc
		28.8	Split peaks of Bcc
		57.6	Split peaks of Bcc
		86.4	Bcc alloy



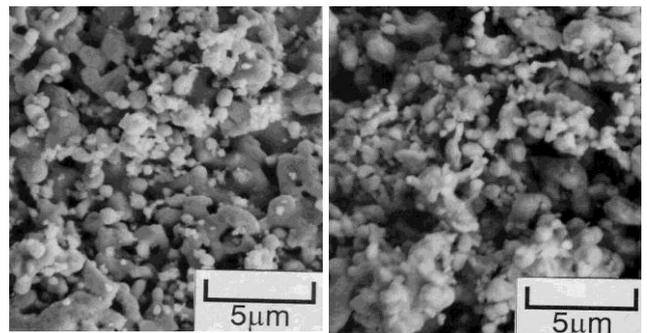
**Fig. 3:** Impurity contents in Nb-Ti powder obtained at 1273K.



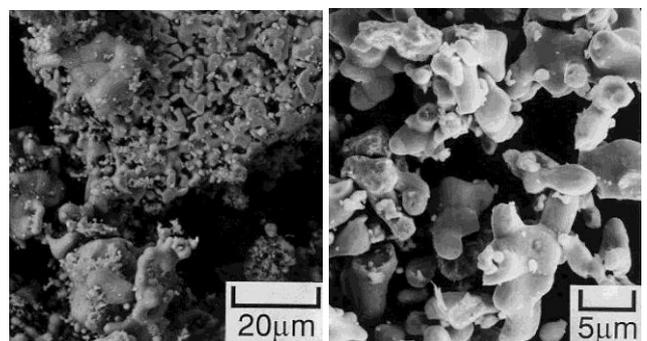
(A) Co-precipitated oxide mixture was reduced by Ca(g).



(B) Co-precipitated oxide mixture was reduced by Ca(l).

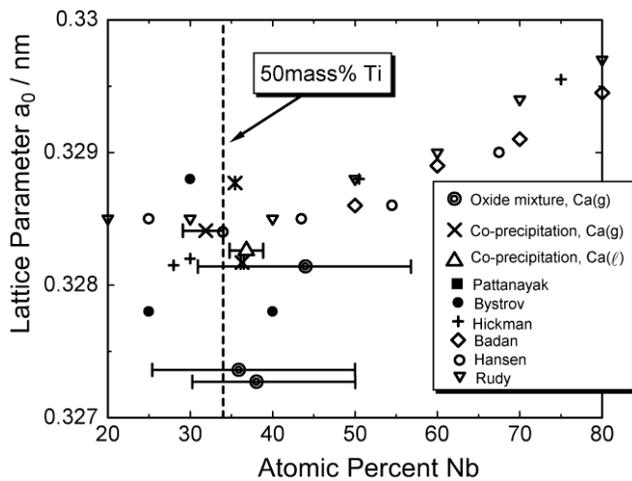


(C) Mechanically mixed oxide was reduced by Ca(g).



(D) Co-precipitated oxide mixture was reduced by Ca(l).

**Fig. 4:** SEM images of Nb-Ti powder obtained at 1273K. The reaction time was (a) 86.4 ks and (b) 28.8 ks.



**Fig. 5:** Compositional dependency of reported lattice parameter. Nb contents in the obtained particles were analyzed by EDX.

particles was within  $\pm 2.8\text{mass}\%$  in all the co-precipitated samples. However, the scatter was over 10% in the samples starting from the mechanically mixed oxides, and in the samples reacting for the shorter time. The powder obtained from the co-precipitated oxide mixture hold the same lattice parameter reported previously in the bulk alloys.

Summarizing the phase change and the compositions in the obtained particles, the sequence of co-reduction can be sketched as follows. The reductant Ca reduces both  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$ , however, the reduction of  $\text{TiO}_2$  delays because of its stronger thermodynamic stability. A part of  $\text{TiO}_2$  forms  $\text{CaTiO}_3$  with CaO that was produced from Nb reduction. When the homogeneity in the starting material was poorer, Nb-rich metallic region was formed in the initial stage of reduction. Ti atoms reduced later should diffuse to this region and make a Nb-Ti alloy. When liquid Ca was applied, the Nb particles preferentially produced disperse in Ca melt, and it takes longer time to complete the Nb-Ti solid solution. Both  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  produce a large amount of CaO, CaO covers the metallic portion. It prevents from alloying if the homogeneity in the starting material was poor.

Therefore, we may conclude that the best combination for Nb-Ti co-reduction process was to reduce the co-precipitated oxide mixture using gaseous Ca. This choice was also favorable for carbon and nitrogen contamination.

#### IV. $\text{CaCl}_2$ ADDITION FOR OXYGEN REMOVAL

The residual oxygen in Nb-Ti powder was evaluated by subtracting the contribution of residual CaO to the analytical oxygen content. It was not lower than 0.8mass%, while the theoretical estimation under Ca-CaO

equilibrium is 0.037%, supposing the ideal solid solution in Nb-Ti system. CaO film on the Nb-Ti particles may delay the deoxidation process.

In order to remove the solid CaO layer covering Nb-Ti particles,  $\text{CaCl}_2$  was added on Mo tray. CaO can dissolve in  $\text{CaCl}_2$  molten salt to about 20mol%CaO at 1273K [8,9]. Supposing that all the produced CaO can dissolve in  $\text{CaCl}_2$ , the requested amount of  $\text{CaCl}_2$  was charged. The impurity Ca in Nb-Ti alloy became 0.2mass%Ca, while it was 1.25% without  $\text{CaCl}_2$ . The residual oxygen in the powder was evaluated as 0.15mol%, approaching to the practical level of superconducting wire.

The concept of this deoxidation have been applied to titanium to remove oxygen to 10 ppm level[10]. Because the oxide mixture was exposed to the molten  $\text{CaCl}_2$ , however, the composition in the obtained Nb-Ti powder was deviated in  $\pm 10\text{mass}\%$ . The compositional control will be given by reducing the amount of  $\text{CaCl}_2$  addition.

#### V. CONCLUSION

A co-reduction process for Nb-50mass%Ti alloy powder was examined experimentally. Two kinds of oxide mixture ( $\text{Nb}_2\text{O}_5+\text{TiO}_2$ ) were reduced at 1273 K by gaseous Ca or liquid Ca. Ca gas was favorable to reduce the contamination of impurity such as carbon. The anhydrated co-precipitation from the aqueous solution involving  $\text{Nb}^{5+}$  and  $\text{Ti}^{4+}$  formed the better uniformity in the obtained alloy powder. The addition of  $\text{CaCl}_2$  decreased the residual oxygen to the level of 0.15mass% because the by-product CaO covering the product could dissolve in the molten  $\text{CaCl}_2$ .

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