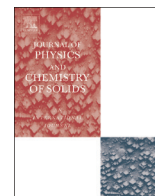




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# Niobium powder synthesized by calciothermic reduction of niobium hydroxide for use in capacitors

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## ABSTRACT

Metallic niobium powder was produced for applications in electric capacitors via calciothermic reduction of niobium hydroxide in molten  $\text{CaCl}_2$ . Sub-micrometer spherical metallic particles with coral-like morphologies reflected the particle size of the starting oxide powder. A fine powder was obtained from the mixtures of niobium hydroxide and  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$ , respectively.

Sintered pellets of the metallic powder showed a higher capacitance (CV) than those of the simply reduced powder without pre-treatment, because the shrinkage during sintering was smaller. The CV was as large as that of commercially sintered pellets for tantalum capacitors. Therefore, this niobium powder would act as a higher-voltage capacitor by applying chemical anodic treatment at higher voltages, and lower oxygen content in the reduced powder could realize a lower leak current.

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## 1. Introduction

Tantalum (Ta) powder is primarily utilized for the production of capacitors in electronic devices commonly found in automobiles, cellular phones, personal computers, and gaming devices. However, Ta powder tends to be more expensive because of the rarity of its ores and the specificity of its accumulation. Soon it will be difficult to respond to the market requirements for cheaper electronic devices.

Niobium (Nb) powder is an attractive alternative of Ta powder, because Nb and its oxide have similar properties to those of Ta and its oxide, and because Nb ore is stably supplied at a reasonable price [1]. High purity Nb powder can be produced by the reduction of  $\text{K}_2\text{NbF}_7$  by liquid sodium (Na) in molten salts, [2] or by the reduction of  $\text{Nb}_2\text{O}_5$  by magnesium (Mg) vapor or  $\text{Mg} + \text{H}_2$  gas [3–6], for example. The first method is similar to the method used in the preparation of Ta powder where  $\text{K}_2\text{TaF}_7$  is reduced by liquid Na [2,7–10]. Applying the current technologies in the Ta industry for Nb powder preparation may be technically facile. Notably, the particle size distribution and morphology of Nb powder will be controlled by certain operating conditions such as the mass balance between the molten salt and the raw material, stirring during

the reaction, and feeding conditions of the raw materials [2,7–10]. However, with this method, the production cost of Nb powder will become similar to that of Ta powder. As a result, the price of Nb powder will also become high.

The latter method (Mg reduction) can produce fine Nb particles corresponding to the starting oxide particles [3–6]. However, it is difficult to control the grain size distribution and morphology so that they are suitable for applications in capacitors. This is partially because the significant exothermal heat that accompanies the chemical reaction is not released from the reaction field and the sintering of the produced particles becomes locally significant.

Powders used for capacitors should be very fine because a larger surface area can guarantee a larger capacitance. The authors propose to replace Mg with calcium (Ca) in the reduction process. Specifically, calciothermic reduction in molten  $\text{CaCl}_2$  was utilized to produce fine Ta and Nb powders directly from  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ , respectively [11–17]. Note that these oxides are much cheaper than  $\text{K}_2\text{TaF}_7$  and  $\text{K}_2\text{NbF}_7$ , respectively.

The overall reaction in the calciothermic reduction could be given as follows:



Thermodynamically Ca was selected as the reductant because of its strong affinity to oxygen [18]. The coexistence of molten  $\text{CaCl}_2$  effectively enhanced the direct reduction of the oxides

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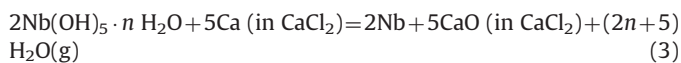
because the film of the reaction by-product, CaO, can be removed by dissolution into liquid  $\text{CaCl}_2$  [19,20]. Residual oxygen in the reduced metal can be eliminated by the lower activity of CaO in molten  $\text{CaCl}_2$ . The coexistence of liquid  $\text{CaCl}_2$  can effectively release exothermic heat to the bulk and suppress the severe sintering of the produced particles during the reduction process [19,20].

The simple reactions shown in Eqs. (1) and (2) successfully produced fine powders with low oxygen contents, and the spherical particles were slightly sintered like a coral [11–16]. This powder morphology was similar to that observed in the conventional Na reduction of  $\text{K}_2\text{NbF}_7$  [7–10]. The coral structure was also reported in the calciothermic reduction from  $\text{TiO}_2$  [11,19,20]. This is probably because the skeleton of oxide particles was preserved after the removal of oxygen from the oxide particles. Superior conductivity and a large capacitance are expected in capacitors with lower oxygen concentrations and larger particle surfaces because individual fine particles are connected with good electrical conductivity [16,17].

In addition to Eqs. (1) and (2), Okabe et al. [12] reported a unique mechanism that the reaction in  $\text{CaCl}_2$  melt could be electrochemically mediated by electron transfer through the external circuit, and that the electron conductive media such as a metallic lead between the oxide and reductant could accelerate oxygen removal from the oxide. When the reductant was electrically separated from the oxide, the morphology did not change significantly [13], and this work will examine the effects of calciothermic reactions by separating from the electron mediated reaction and by considering the practical application.

In the mining industry, raw oxides in non-ferrous metallic ores are generally treated in wet chemical processes to remove impurities [1,2]. Intermediate products such as amorphous hydroxides are normally served for oxide preparation or conversion processes to second intermediate products such as  $\text{K}_2\text{NbF}_7$ . Hydroxide is seldom supplied as a raw material for direct reduction. This is probably because the volume of hydroxide per single metallic atom is large and because excess reductant is needed to remove hydroxide ions. However, the reduction of hydroxide has the potential to produce very fine particles if the skeleton of the hydroxide, with a density lower than that of oxide, can be maintained even after the reduction.

The purpose of this work is to investigate the calciothermic reduction of non-crystalline hydroxides in molten  $\text{CaCl}_2$  with some pre-treatment. The morphologies of the obtained powder as capacitors were studied. A characteristic feature of this method is the well-isolated fine powder preparation. The apparent chemical reaction can be given as Eq. (3):



where a significant amount of exothermic heat (673 kJ/mol Nb at  $n=0$  and 1173 K [15]) is released. The local sintering or coarsening of the particles due to the exothermic heat will be minimized via thermal transfer to the surrounding molten salt. As a result, an interesting morphology will be realized in that needle-, branch-, or plate-like particles and it will coexist with fine and spherical particles. The forming conditions and the electric properties of these unique morphologies will be reported and compared to the calciothermic reduction of  $\text{Nb}_2\text{O}_5$  and its coral-like Nb powder [11,12,16,21]. It is noted that the required quantity of Ca per Nb atom is 2.5 mol both in Eqs. (2) and (3).

The preferential reaction site, whether the reduction occurs in the molten salt or on the oxide particles, is also interesting. Yuan and Okabe [22–24] showed the possible mechanism of reduction

in  $\text{KCl-NaCl-MgCl}_2\text{-DyCl}_2$  melt that the reductant,  $\text{Dy}^{2+}$ , dissolved in the melt can react with Ta ions also dissolved in the melt to form Ta powder. They reported that the reaction product,  $\text{Dy}^{3+}$ , is reduced by either electrochemical or magnesiothermic reduction at the cathode and regenerated to reductant  $\text{Dy}^{2+}$ . The authors thought that their unique idea ( $\text{Dy}^{2+}/\text{Dy}^{3+}$ ) in  $\text{MgCl}_2$  based salt may be expanded to the other molten salt such as  $(\text{Ca}/\text{Ca}^{2+})$  in  $\text{CaCl}_2\text{-CaO}$  melt. Although Ca metal can dissolve in a  $\text{CaCl}_2$  melt and react with the oxide, most previous studies reported that the reduction occurs on the surface of the solid oxide particles.

## 2. Experimental

### 2.1. Pre-treatments and procedures

High purity niobium hydroxide was supplied by Zhongguo-guoyoungong-sijiatezhi in China. Hereafter, it will be referred to as raw material Type I. This white powder was treated in the following three ways prior to reduction to yield raw material Types II, III, and IV.

Raw material Type II was produced from raw material Type I by sol-gel dehydration. Raw material Type I was mixed with hydrous  $\text{Ca}(\text{OH})_2$  (99.9% in metallic purity) and distilled water in a molar ratio of raw material Type I:  $\text{Ca}(\text{OH})_2:\text{H}_2\text{O}=1:1:2$ , where the chemical formula of the raw material Type I was assumed to be  $\text{Nb}(\text{OH})_5$ . The pH of the gel was 13–13.5. This white gel was filled in a niobium crucible (75 mm in ID., 65 mm high), and heated at 573 K for 3.6 ks and subsequently at 773 K for 3.6 ks in vacuum evacuated continuously by rotary pump. There was no apparent shrinkage during heating. After cooling, the sample was pulverized in an agate mortar and used as raw material Type II.

Raw material Type III was prepared as follows: the calcined CaO (99.9%) and raw material Type I were mixed in a 1:1 M ratio and pressed into cylindrical pellets (5 mm in diameter, 10 mm high). The pellets were heated at 773 K for 3.6 ks under vacuum evacuated continuously by a rotary pump. Only raw material Type III was utilized as the pellets for reduction.

Raw material Type IV was prepared as follows: NaOH was used in the sol-gel method as the alternative of  $\text{Ca}(\text{OH})_2$  utilized to produce raw material Type II. The mixing molar ratio of  $\text{Nb}(\text{OH})_5:\text{NaOH}:\text{H}_2\text{O}$  was 1:2:2. The white gel was similarly heated at 573 K for 3.6 ks and at 773 K for 3.6 ks under vacuum. The pulverized sample was used as raw material Type IV.

Oxide Type V is niobium oxide,  $\text{Nb}_2\text{O}_5$  (99.9%), which was supplied by Mitsui Metals Ltd.

### 2.2. Procedures for reduction

Detailed procedures for the reduction, sintering, and evaluation of electric properties were previously reported for Ta powder [11,13–17]. The procedures used in this study were based on these reports, and a brief outline and some modifications are given below.

Metallic calcium lumps (99.8% pure),  $\text{CaCl}_2$  powder (99.9%), and one of the raw materials, were filled in the Nb crucible in that order. The crucible was heated in stainless steel vessel, as shown in Fig. 1.

At a reaction temperature above the melting points of Ca and  $\text{CaCl}_2$ , the lighter Ca flows upwards and the heavier raw material sinks on the bottom of crucible due to the difference in density, as illustrated in Fig. 1. The reverse arrangement of the starting materials was reported to enhance the calciothermic reduction of  $\text{Ta}_2\text{O}_5$  to form broccoli-like powders [14–17]. Those samples were reacted at 1153 K for 7.2 ks in an Ar gas atmosphere, and the molar ratio of the raw material: Ca reductant: $\text{CaCl}_2$  solvent was set as

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