

# Niobium Powder Production in Molten Salt by Electrochemical Pulverization

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The electrochemical-pulverization technique of bulk niobium was investigated with the purpose of developing a new process for the production of fine niobium powder for use in electronic devices. A niobium rod produced by aluminothermic reduction (ATR-Nb) was immersed in NaCl-KCl-MgCl<sub>2</sub>-DyCl<sub>2</sub> molten salt at 1000 K and electrochemically dissolved in the molten salt. The dissolved niobium ions were *in-situ* reduced by Dy<sup>2+</sup> ions in the molten salt, and niobium powder with an average particle size below 1 μm was successfully obtained. The optimum parameters for producing high-purity niobium powder with controlled morphology are currently under investigation.

## 1. Background

Recent trends in the downsizing of electrical appliances such as laptop computers and cellular phones have accelerated the demand for high-performance capacitors. Due to this trend and the fact that tantalum capacitors have the greatest capacity per unit volume and are thermally stable as compared to other capacitors, the production volume of tantalum metal powder has increased dramatically in the last 20 years [1, 2]. Currently, more than 50% of tantalum resources are used in tantalum capacitors. However, the production volume of tantalum metal powder for capacitors is limited because the tantalum resource in the earth's crust is scarce and tantalum is one of the valuable metals. In the year 2000, the balance between the demand and supply of tantalum ore collapsed due to a strong demand in the market. The price of the ore increased six-fold and tantalum capacitor manufacturers encountered a material crisis [3].

Considering this situation, extensive research on the production of niobium powder as a substitute for tantalum in capacitors is being carried out [1, 2, 4]. This is primarily due to the fact that the chemical and physical properties of niobium are very similar to those of tantalum. In recent years, "niobium capacitors" and "niobium oxide capacitors" have been successfully produced on a commercial scale and their potential demand is increasing.

Tantalum powder for capacitors is currently produced by the sodiothermic reduction of halide salts (potassium heptafluorotantalate, K<sub>2</sub>TaF<sub>7</sub>), which is commonly termed the Hunter process (see Fig. 1 (a)) [5]. This process is suitable for producing high-purity tantalum with controlled powder morphology. However, it requires a large amount of molten salt as a reaction medium that is referred to as a "diluent." Furthermore, this process lacks the flexibility of being scaled up, and it is difficult to make it continuous. Currently, a majority of metallic niobium and its alloys are produced by the aluminothermic reduction (ATR) of niobium oxide in an electric furnace. This process is economically suitable for large-scale operations but not for producing fine powder with controlled purity for electronic applications.

Serjak *et al.* recently carried out research on the metallothermic reduction of niobium oxide for producing niobium powder for the capacitors [4]. In general, it is difficult to control purity and morphology of metal powders by the conventional metallothermic reduction of oxides, but they



## 2. Niobium powder production by utilizing electrochemical pulverization (EP) of niobium rod

Fig. 1 (b) shows the principle of the EP process investigated in this study. Niobium feed in the form of a rod, produced by the aluminothermic reduction (ATR-Nb), is immersed in NaCl-KCl-MgCl<sub>2</sub>-DyCl<sub>2</sub> molten salt and it serves as an electrode (anode). It is then polarized anodically by using an external power source and is electrochemically dissolved into the molten salt. The dissolved niobium ions are *in-situ* reduced by Dy<sup>2+</sup> ions in the molten salt and fine niobium powder is produced.

The experimental procedure and apparatus for carrying out the EP process is shown in Figs. 2 and 3, respectively. As shown in Fig. 2, dysprosium (Dy) metal lumps (30.5 g) and silver shots (20.0 g) contained in a stainless steel alloy holder (see Fig. 3) were immersed in the NaCl-32 mol%KCl-11 mol%MgCl<sub>2</sub> molten salt (approximately 1300 g), and DyCl<sub>2</sub> was *in-situ* produced by the redox reaction between dysprosium metal and MgCl<sub>2</sub> salt. Magnesium (Mg) produced by the redox reaction was absorbed by the silver, and the Mg-Ag liquid alloy electrode was formed and it served as the cathode. In order to analyze the electrochemical properties of molten salts, cyclic voltammetry (CV) was performed before and after the addition of dysprosium metal to the molten salt. After confirming the existence of the redox couple of Dy<sup>2+</sup>/Dy<sup>3+</sup> in the molten salt, the electrochemical pulverization of the niobium rod (diameter  $\phi$ : 10 mm, depth: 10 mm) was conducted by applying current (current: 2 A, time: 31 ks) through an external power source. The electrochemical property of the molten salt after the EP experiment was measured by CV. It was found that the electrochemical properties of the molten salt remained constant before and after the EP experiment, which demonstrated that Dy<sup>2+</sup> was regenerated during the experiment and was not consumed. These results indicated that the reaction medium could be re-used for multiple runs of EP of the niobium rod.

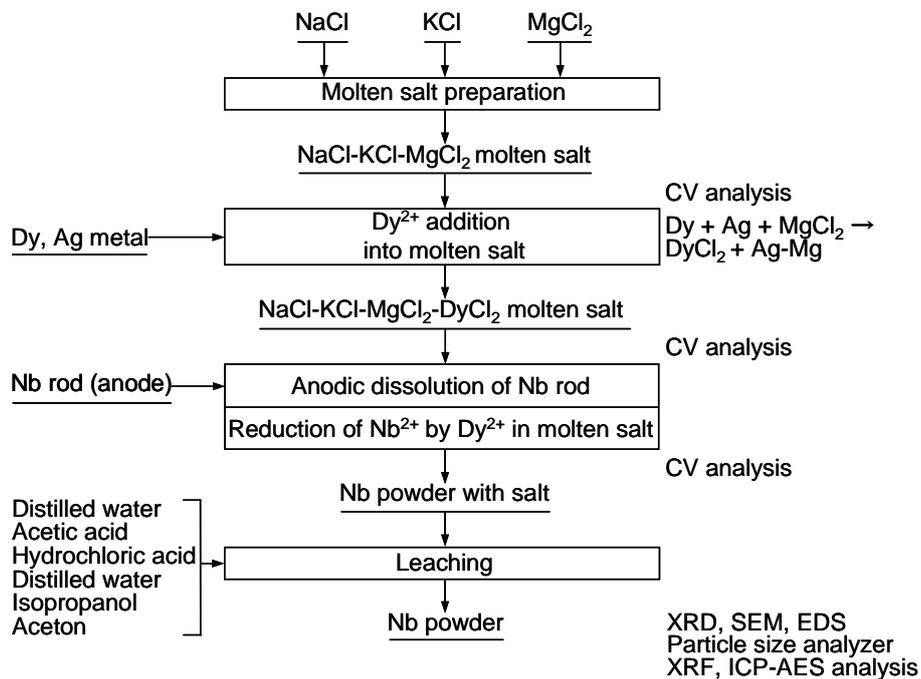


Fig. 2 Flowchart for niobium powder production by the EP process.

Presently, niobium powder with an average particle size below 1  $\mu\text{m}$  has been successfully obtained. Fig. 4 shows a representative scanning electron microscopic (SEM) image of the niobium powder obtained after the removal of salt by leaching. The optimum parameters for producing high-purity powder with controlled morphology are currently under investigation.

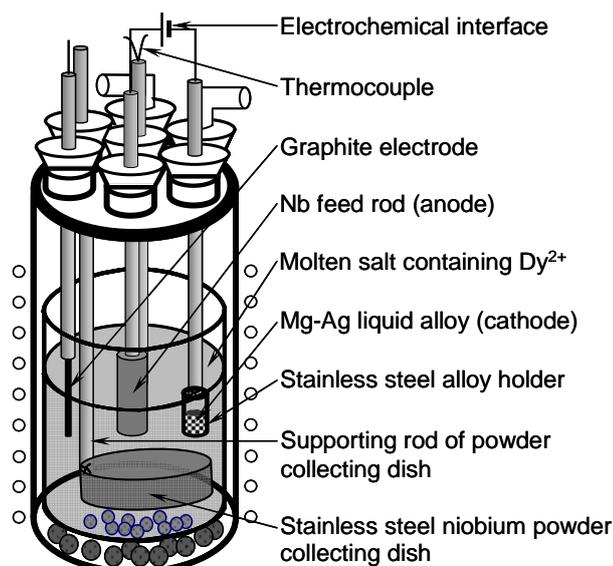


Fig. 3 Schematic illustration of the experimental setup for electrochemical pulverization (EP) of niobium rod. Cyclic voltammetry for NaCl-32 mol% KCl-11 mol% MgCl<sub>2</sub> molten salt was carried out before and after Dy metal addition.

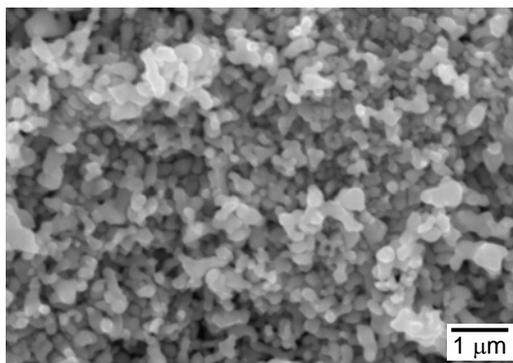


Fig. 4 SEM image of niobium powder produced by the EP technique.

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