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Formation of broccoli-like morphology of tantalum powder

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Abstract

"Broccoli"-like morphology of Ta powder was found when Ca reduces Ta_2O_5 in the molten $CaCl_2$. It consisted of fine particles and branches, and it was different from the conventional spherical particles. The formation of this morphology depended on the stacking methods of the starting materials. Eight types of filling methods proved that the branch was formed when the CaO-enriched region was locally produced near the oxide.

Keywords: Calciothermic reduction; Tantalum oxide; Powder morphology; Tantalum powder; Molten salt

1. Introduction

Surface oxidation of the fine tantalum powder forms an excellent capacitor because the combination of the tantalum oxide film and the bulk metal gives a good capacitance and electric conductivity. The better conductivity and the larger capacitance are expected by reaching a lower oxygen concentration in the bulk and a larger particle surface. The larger surface area is generally obtained by making the powder finer, but the individual particles should be connected for conductivity.

Tantalum powder is industrially produced by sodium reduction of K_2TaF_7 in the molten salt consisting of KCl-NaCl-NaF. Its grain size and its morphology are controlled by the amount of charge, stirring of the molten salt and the injection of raw materials [1]. The solidified salt is removed after cooling, the reduced powder is then deoxidized by Mg vapor at high temperatures, and the spherical particles after sieving are again sintered to connect the particles in the capacitor form. A more compact process is requested for energy saving and waste management without any fluoride.

Because Ta_2O_5 costs about 1/6 of K_2TaF_7, the calcium reduction of Ta_2O_5 has been proposed aiming at the preparation of fine Ta powder, by reduction, deoxidation and sintering in one-step [2]. Thermodynamically Mg or Ca was selected as the reductant [3–6]. In Ca reduction, for example, the by-product CaO adheres to the formed Ta particles as a film, as shown in Fig. 1(a), and it is captured among the sintered particles. It became an obstacle to eliminate the residual oxygen from the metallic particles [2,5,6].

However, molten $CaCl_2$ can enhance the reduction mainly because the CaO at the reaction interface dissolves into the $CaCl_2$ melt [2,6].

$$Ta_2O_5 + Ca\,(\text{in } CaCl_2) = Ta + CaO\,(\text{in } CaCl_2) \qquad (1)$$

where the reductant Ca also dissolves in the molten $CaCl_2$, as shown in Fig. 1(b). The solubilities of CaO and Ca in $CaCl_2$ around 1200 K are about 20 and 4 mol%, respectively [7–12]. Because the exothermic reaction becomes milder and more homogeneous by $CaCl_2$ addition, the coarsening of the formed Ta particles is suppressed. In addition, the residual oxygen in the reduced metal can be decreased by the low activity of CaO in the molten $CaCl_2$.

A previous study showed that 4000 mass ppm oxygen in Ta was attained from the starting Ta_2O_5 [2]. It was a level similar to that by the conventional Na reduction of K_2TaF_7. The spherical Ta particles were slightly sintered like a coral, and

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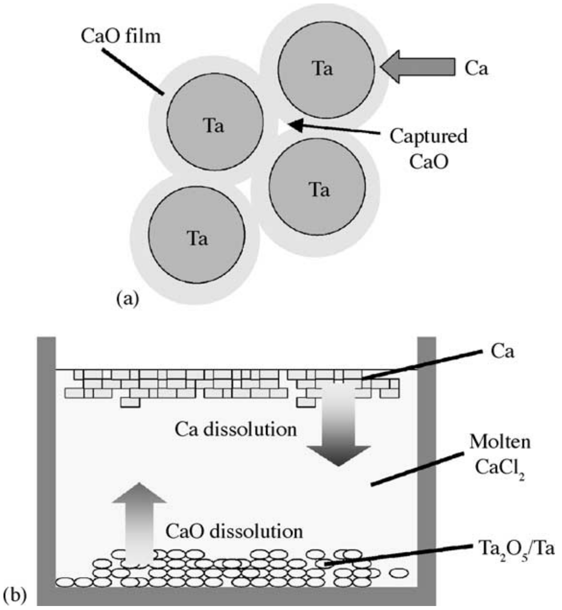

Fig. 1. Calciothermic reduction of Ta_2O_5. (a) Without $CaCl_2$ and (b) in $CaCl_2$.

the particle size was equivalent with that of the starting oxide. A similar morphology was observed also in the Ca reduction of TiO_2 or Nb_2O_5 [2,13–18]. This is probably because the skeleton of oxide particles was preserved even after oxygen removal from the oxides.

During the successive work of Ca reduction of Ta_2O_5 in molten $CaCl_2$ [2], we found an interesting morphology, which looked like “broccoli”. It consisted of long and thin branches and spherical fine particles, and it was different from the previous coral-like powder. The purpose of this work is to report the forming conditions and mechanism of this broccoli-like morphology.

2. Experimental procedures

2.1. Reduction

The raw materials are Ta_2O_5 powder (Mitsui Metals, 99.9% in metallic purity), Ca lumps (Hitachi Alloy, 99.8%, a few mm in size), anhydrate $CaCl_2$ powder (Soekawa Chemicals, 99.9%), CaO powder (Wako Chemicals, 99.5%, calcined in air at 1273 K for a day) and Ta powder (Cabot Supermetals, 99.8%). They were filled in a Ta crucible (>99.9%, 75 mm in diameter, 65 mm in depth) as shown in Fig. 2. The pure Ta crucible was used to avoid the contamination. The total amounts of charge were 190–230 g. Because the experimental apparatus and procedures for the reduction were the same as in the previous report [2], only a brief outline and the differences will be given here.

The lighter Ca liquid flows on the heavier molten $CaCl_2$ because of density difference, and the heavier Ta_2O_5 powder settles on the bottom of Ta crucible. Note that the formed Ta is the heaviest.

In the setup of type-I as shown in Fig. 2, the Ca lumps were set on the bottom of the crucible, and the $CaCl_2$ powder was filled on the Ca. The Ta_2O_5 powder was finally placed on the top surface of the $CaCl_2$ powder. After melting of $CaCl_2$ above 1048 K, its depth became about 35 mm. The Ta_2O_5 powder and the liquid Ca were expected to meet together in the molten $CaCl_2$. The arrows in Fig. 1 show the moving directions of Ca and Ta_2O_5 after the melting of $CaCl_2$. This type-I was used in the previous report [2].

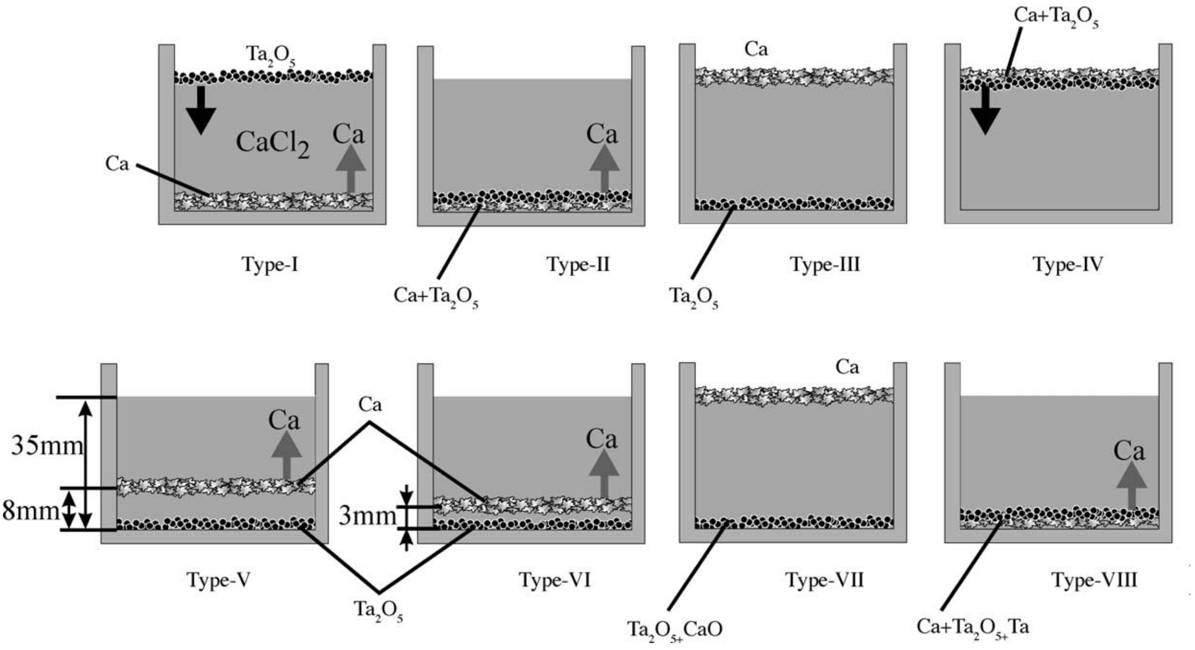

Fig. 2. Setup of starting materials in the Ta crucible. The arrows show the moving direction after melting of $CaCl_2$ and Ca.