Formation of Broccoli-like Morphology of Ta Powder

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Surface oxidation of the fine tantalum powder forms an excellent capacitor. The better conductivity and the larger capacitance are expected by getting the lower oxygen concentration in the bulk and the finer particle. Tantalum powder is industrially produced by sodium reduction of K_2TaF_7 in the molten salt consisting of KCl-NaCl-NaF. A more compact process is requested for energy saving and waste management without any fluoride.

The calcium reduction of Ta_2O_5 in molten $CaCl_2$ has been proposed aiming at the preparation of fine Ta powder, the deoxidation and the sintering in one-step [1] where 4000 mass ppm oxygen in Ta was attained from the starting Ta_2O_5. The spherical Ta particles were slightly sintered like the coral, and the particle size was equivalent with the conventional method. As the successive work of Ca reduction of Ta_2O_5 in the molten $CaCl_2$, we found an interesting morphology, which looked like “broccoli”. It consisted of the long and thin branches and the 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.

Ta_2O_5 powder, Ca lumps and anhydrate $CaCl_2$ powder were filled in the Ta crucible as shown in Fig.1. The lighter Ca liquid floats up on the heavier molten salt because of density difference, and the heavy Ta_2O_5 powder is settled on the bottom of the Ta crucible. In the setup of Type-I, the Ta_2O_5 powder was set on the bottom of the crucible, and the $CaCl_2$ powder was filled on the Ta_2O_5. The Ca lumps were finally placed on the top surface of the $CaCl_2$ powder. In the setup of Type-II, both the Ta_2O_5 powder and the Ca lumps were set below the $CaCl_2$ powder. In the setup of Type-III, CaO powder was mixed with Ta_2O_5 powder on the bottom.

After the reduction for 7.2 ks at 1223 K, the oxygen concentration of the powders was in the range of 0.3-1.0 mass pct. All the powder contained the spherical particles commonly. They combined each other like the coral structure as reported [1]. Especially the powder of Type-I consists of only the fine particles as shown in Fig.2. A characteristic morphology was, however, found in Type-II and Type-III as shown in Fig.2. In addition to the coral-like structure, a strange structure like “broccoli” was formed. This consists of the branches and the fine particles adhered to the branch. The branches often look like one-dimensionally aligned chains of many particles, and they have several branches.

The case of broccoli formation will be here explained from the aspect of local CaO concentration. The dissolution rates of CaO are slow at the studied temperature range, especially in the higher concentration range of CaO. In Type-I, the CaO concentration increases gradually and steadily, because the dissolved Ca in $CaCl_2$ reduces Ta_2O_5 slowly, and because no physical contact occurs between Ca droplets and Ta_2O_5 powder. In Type-II, the reduction starts just after melting of Ca at the bottom of the crucible, where the CaO concentration near the oxide rises suddenly. It may raise the CaO concentration above the saturation value. Then the CaO concentration decreases gradually. In Type-III, the initial CaO concentration was locally high near the Ta_2O_5 powder. The difference between Type-I and Type-II,III was only the existence of highly concentrated CaO. Here we conclude experimentally that a high CaO concentration in the molten $CaCl_2$ near the oxide is the requisite of the broccoli formation.

References

[1] M. Baba, Y. Ono and R.O. Suzuki, J. Phys. Chem. Solids, (2004) accepted for publication.

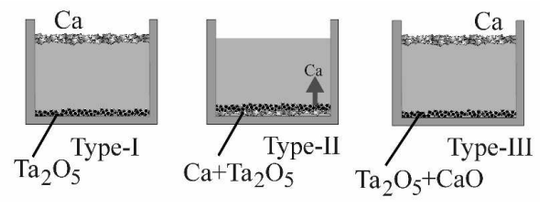

Fig.1. Setup of starting materials in the Ta crusible.

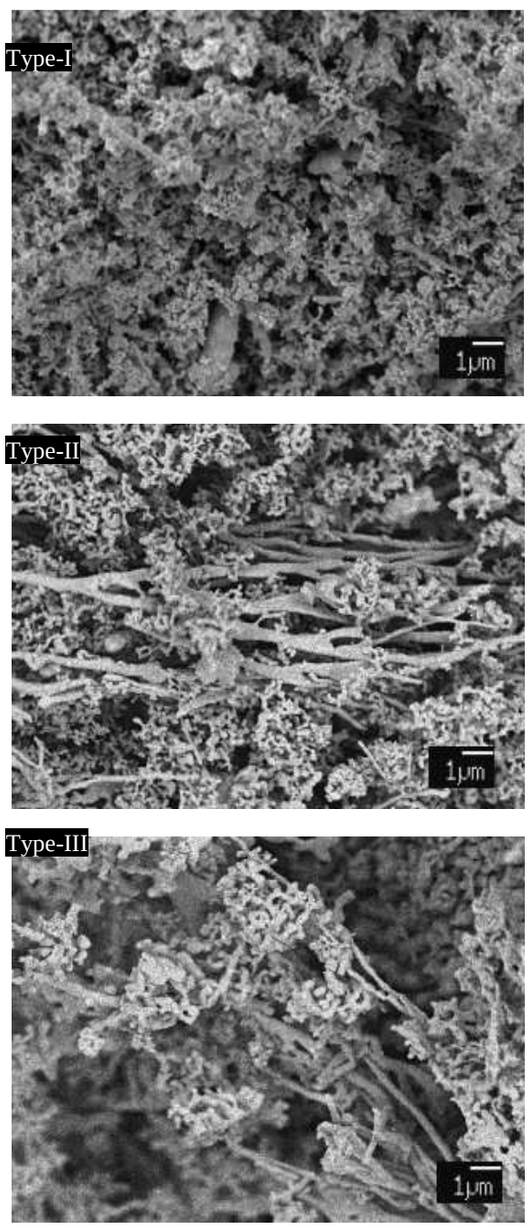

Fig.2. SEM images of Ta powders of Type-I-III.