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Influence of the Particle Size Distribution of Potassium Heptafluorotantalate on the Characteristics of Sodium-Reduced Tantalum Powders

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Abstract—Two versions of heterophase sodium-thermic reduction of potassium heptafluorotantalate were studied. One version implies initiation of the reaction in a homogeneous mixture of solid K_2TaF_7 and sodium flux, and the other, supply of solid K_2TaF_7 onto the surface of liquid sodium occurring above the molten halides. The surface area of the tantalum powder was correlated with the K_2TaF_7 particle size. The formation mechanisms for the tantalum powder particles were discussed for different reduction procedures. The conditions for preparation of powders with the specific surface area of ca. 4 $m^2 g^{-1}$ were identified.

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Electrolytic tantalum capacitors with porous anodes have found radioelectronic application for more than 50 years [1] and are increasingly in use owing to their unique characteristics, above all reliability, low equivalent consecutive resistance, and high specific charge. The tantalum powders used for manufacturing capacitor anodes are characterized by ever increasing surface area, which ensures steady growth of the specific charge, essential for miniaturization of electronic devices [2].

These powders are currently prepared primarily by sodium-thermic reduction of potassium heptafluorotantalate (PFT) in modes utilizing reactants in different aggregation states.

Here, we explored the possibility to increase the surface area of the powders in "heterophase" reduction of potassium heptafluorotantalate, in which the reaction is initiated between solid PFT and liquid sodium.

EXPERIMENTAL

The process was run in two versions, of which one implies initiating the reaction in a homogeneous mixture of solid potassium heptafluorotantalate and neutral addition (ultrapure grade potassium chloride) with sodium. For details on the experimental technique and equipment, see [3]. In our experiments we used PFT characterized by a narrow particle size distribution with needle-shaped crystals whose cross-sectional area decreased proportionally to the crystal length. In the other version of the process, crystalline potassium heptafluorotantalate was supplied onto the surface of a liquid sodium layer above a molten eutectic mixture of sodium and potassium chlorides. We used chemically pure-grade NaCl and KCl which were preliminarily dehydrated in air at 600°C for 6 h.

The process was implemented in a reactor designed for preparation of up to 1.5 kg of tantalum powder in one experiment [4]. The beaker containing a mixture of alkaline metal halides was placed into a retort reactor which was hermetically sealed, evacuated, filled with argon, and heated till melting of the salts. This was followed by pouring the melt surface with sodium from a container in the amount required for reduction of the desired amount of PFT, taken in a 5% excess with respect to the stoichiometric amount. The PFT–NaCl mixture (molar ratio NaCl : K_2TaF_7 = 3) was supplied from a dosing bin fixed on the branch pipe of the reactor cover. Potassium heptafluorotantalate was supplied into

Table 1. Characteristics of the powders prepared by reduction of a homogeneous feed mass in relation to the K_2TaF_7 particle size. Anode sintering temperature 1450°C

Average particle size of K_2TaF_7, μm	γ, g cm^{-3}	S_{UGP}, m^2 g^{-1}	Δdd^{-1}, %	Q, μC g^{-1}
200	0.78	0.7	1.7	27250
100	0.64	0.9	5.8	31370
25	0.50	1.3	8.5	37570

the melt at a rate varied within 60–115 g min^{-1}.The melt temperature during reduction was maintained within 700–850°C.

To prepare potassium heptafluorotantalate with crystals of different sizes, recrystallized K_2TaF_7 with > 1mm particles, containing <0.001 wt% metal impurities, was subjected to cyclic heating to 250°C in an argon atmosphere, and this was followed by cooling to 100°C. This led to reduction in size of the primary crystals via polymorphic transformation at 203°C [5]. This heat treatment yielded PFT represented by crystal fragments with a close to equiaxial shape of the particles. It was characterized by the following particle size distribution, %: ≥315 μm 4, <315...≥160 μm 28, <160...≥90 μm 34, <90 μm 34. Heat-treated potassium heptafluorotantalate and the fractions isolated therefrom served as the initial material for reduction.

When the reduction was complete, the reaction mixture was cooled to room temperature, taken out of the beaker, and crushed into <5 mm particles. Next, the powder was washed with water taken in the amount required to remove salts [6]. The specific surface area of the powder was determined by the vacuum gas permeability method on a UGP-2 instrument (S_{UGP}) and by the BET static adsorption method on a Flowsorb II 2300 instrument (S_{BET}); the bulk density γ was estimated in accordance with State Standard (GOST) 19440. The particle size distribution in the < 40 μm fraction was examined on a Lumosed photosedimentometer available from Retsch. The anodes with the density of 3.5 g cm^{-3} for determining the electric characteristics were manufactured by methods commonly used for capacitor manufacture.

In reduction of a homogeneous feed mass comprised of PFT, halides, and sodium there was a good contact between the reactants, and the reaction began at 120–200°C, i.e., between liquid sodium and solid potassium heptafluorotantalate. The temperature achieved in the reaction was 800–880°C. Table 1 lists the specific surface area of the tantalum powder, radial shrinkage Δdd^{-1}, and specific charge of anodes Q in relation to the K_2TaF_7 particle size. Table 2 presents the particle size distribution of the powders obtained by reduction via supply onto the molten sodium surface of heat-treated potassium heptafluorotantalate and its individual fractions. The tabulated data suggest that, in reduction of K_2TaF_7 with <315 μm crystals, the resulting powder was comprised entirely of <40 μm particles. At the same time, in the presence in PFT of the >315 μm fraction there was a significant number of >40 μm powder particles.

The difference in the patterns of variation with the heptafluorotantalate particle size for the surface area of the tantalum powders prepared by different versions of the heterophase reduction procedure suggests a substantial

Table 2. Characteristics of the powders prepared by reduction on the molten sodium surface in relation to the K_2TaF_7 particle size and supply rate. Anode sintering temperature 1350°C

K_2TaF_7 particle size, μm	K_2TaF_7 supply rate, g min^{-1}	Content of <40 μm fraction, %	γ, g cm^{-3}	S_{BET}, m^2 g^{-1}	Δdd^{-1}, %	Q, μC g^{-1}
Initial	90	94.8	0.91	1.5	4.4	48050
≥315	90	92.5	1.17	0.7	3.2	26400
<315	90	100	0.77	3.2	11.9	49200
<315...≥160	75	100	0.75	3.3	8.8	49700
	80	100	0.75	3.3	8.3	52400
<160...≥90	60	100	0.65	3.0	8.5	55800
	115	100	0.65	4.1	8.8	54000
<90	85	100	0.60	4.1	11.2	57400
	90	100	0.60	4.0	11.5	57700

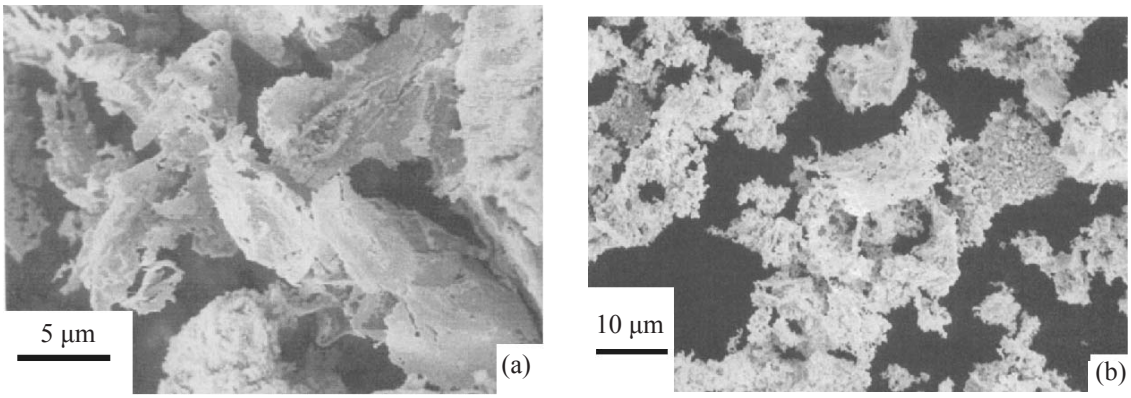

Fig. 1. Morphology of the tantalum powders prepared by (a) reduction of a homogeneous feed mass and (b) supply of K_2TaF_7 onto the molten sodium surface.

difference in their formation mechanism, although in both cases the powders are represented basically by lamellar particles (Fig. 1). In reduction of a homogeneous mixture of potassium heptafluorotantalate and sodium the reaction begins at a fairly low temperature on the surface of the heptafluorotantalate particles. Heat liberation caused their melting into lamellar particles with a relatively smooth surface (Fig. 1a). The specific surface area of the particles with this specific shape is determined primarily by the thickness of the lamellas, which, in turn, varies with the cross-sectional area of the PFT crystal: The thinner the latter, the smaller the thickness of the tantalum powder particles and the larger the specific surface area. As already mentioned, this cross-sectional area is proportional to the crystal length. This is specifically responsible for a substantial increase in the specific surface area of the powder and an increase in the specific charge of the anodes with decreasing average particle size (Table 1).

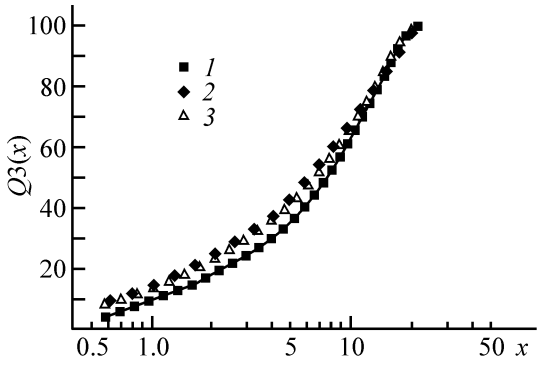

Fig. 2. Cumulative particle size distribution curve $Q3(x)$, %, for <40 μm tantalum powder fraction. K_2TaF_7: (*1*) initial, (*2*) <315...≥ 160 μm fraction, and (*3*) <90 μm fraction.

Table 2 suggests that, in reduction by supply of PFT onto the molten sodium surface, the characteristics of the powder do not strongly vary with the K_2TaF_7 particle size when the average particle size is under 315 μm. This is also validated by the results of photosedimentation analysis of the <40 μm powder fraction (Fig. 2). The reason is that, when getting onto the sodium surface heated to700–800°C, the essentially cold PFT particle is subjected to high thermal stresses and can be destroyed. These stresses are enhanced with increasing temperature because of the reduction reaction proceeding on the particle surface at the site of contact with sodium. The stresses induced in small particles are insufficient for their destruction. This results in the lack of >40 μm particles, as well as of a substantial difference in the specific surface area and in the specific charge of anodes in reduction of different fractions of heptafluorotantalate with <315 μm particles. Destruction of heptafluorotantalate crystals >315 μm in size yields a certain number of large fragments whose size is sufficient for growth of >40 μm tantalum powder particles.

It should be noted that the lamellar particles formed in both cases differ significantly in the surface characteristics. The tantalum powder particles prepared by reduction via supply of PFT onto molten sodium are characterized by a larger surface area (Fig. 1b). This can be treated both as an evidence of partial reduction by sodium vapor above the melt surface and of reduction without complete melting of the PFT particle. In both cases the tantalum particle surface will correspond to the surface roughness of potassium heptafluorotantalate.

From the viewpoint of implementation of the powder surface in capacitor anodes, lamellar powders with

a smoother surface are certainly advantageous. Powders comprised of lamellar particles are characterized by smaller shrinkages in sintering and higher degrees of implementation of the surface in anodes. They are suitable for manufacturing capacitors intended for operation at higher working pressures. Unfortunately, there exist only limited opportunities for increasing the powder surface by heterophase reduction of a homogeneous mixture of heptafluorotantalate with sodium. Because of high reactivity of PFT with <50 μm particles the reaction can begin already during the mixture preparation, virtually at the melting point of sodium. This prevents commercial implementation of the process for preparing powders with a specific surface area of 1.5 $m^2 g^{-1}$. In this context, more promise is offered by heterophase reduction procedure in which potassium heptafluorotantalate is supplied onto the molten sodium surface. With potassium heptafluorotantalate comprised of <315 μm particles this yields tantalum powders with the specific surface area of 3.3–4.0 $m^2 g^{-1}$. These powders constitute a good basis for manufacturing capacitor powders with 50 000 μC g^{-1} charges.

CONCLUSIONS

(1) The potassium heptafluorotantalate crystal size affects the specific surface area of the tantalum powders prepared by different versions of heterophase sodium-thermic reduction: by initiating the reaction in a homogeneous mixture of solid K_2TaF_7 with sodium and by supplying solid K_2TaF_7 onto the surface of liquid sodium occurring above the halide melt. This allowed the formation mechanisms for tantalum powder particles to be proposed for each of the process implementation version.

(2) The supply onto the molten sodium surface of potassium heptafluorotantalate with <300 μm particles allows preparing tantalum powders with the surface area of up to 4 $m^2 g^{-1}$. These powders constitute a good basis for manufacturing high-capacity capacitor powders.

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REFERENCES

1. Taylor, R.L. and Haring, H.E., *J. Electrochem. Soc*., 1956, vol. 103, no. 11, pp. 611–613.
2. Pozdeev-Freeman, Y.*, TIC Bull. June*, 2005, no. 122, pp. 4–8.
3. Orlov, V.M., Miroshnichenko, M.N., and Sukhorukov, V.V., *Zh. Prikl. Khim*., 2006, vol. 79, no. 8, pp. 1233–1237.
4. Kolosov, V.N., Orlov, V.M., Prokhorova, T.Yu., and Miroshnichenko, M.N., *ECS Transactions*, 2007, vol. 3, no. 35, pp. 395–398.
5. Agulyanskii, A.I., Bessonova, V.A., Kuznetsov, V.Ya., and Sklokina, N.F., *Zh. Neorg. Khim*., 1982, vol. 27, no. 3, pp. 679–682.
6. Belyaev, K.Yu., Orlov, V.M., Prokhorova, T.Yu., and Savotkina, M.N., *Tekhnologiya mineral’nogo syr’ya i svoist-va soedinenii redkikh metallov* (Technology of Mineral Raw Materials and Properties of Compounds of Rare Metals), Apatity: Kol’sk. Nauch. Tsentr Ross. Akad. Nauk, 1997, pp. 24–33.