INFLUENCE OF ALKALI HALIDE ADDITIONS ON TANTALUM POWDER PRODUCTION[①]

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ABSTRACT Phase diagrams of K_2TaF_7-NaCl, K_2TaF_7-KCl and K_2TaF_7-NaCl-KCl systems were analyzed in detail. Homologous relations between K_2TaF_7-alkali halide systems and the technical parameters have been put forward, and influence of alkali halide additions on the specific capacity of Ta powder has been studied.

Key words K_2TaF_7 diluent phase diagram molten salt system Ta powder specific capacity

1 INTRODUCTION

The method of K_2TaF_7 reduction with sodium is of great importance in Ta powder production up till now. The reaction is as follows:

$$K_2TaF_7 + 5Na = Ta + 2KF + 5NaF \quad (1)$$

Reaction (1) is violently exoergic. In order to control the reaction rate, the diluents which do not participate in the reaction, e. g. NaCl, KCl, are added with the reactants. The diluents can reduce the melting point(M.P.) and viscosity of the molten salt, improve the characteristics of Ta powder, and especially increase the specific capacity[1].

At present, study on Ta powder is aimed at obtaining high specific capacity. With Ta powder classified, heat-treated properly and mingled with certain elements, the specific capacity of the powder can be increased greatly[2]. But K_2TaF_7 reduction with sodium is the critical process[3]. The species ratio, the diluents and their quantities etc. are also important factors during the reduction.

Based on the analysis of the phase diagrams of K_2TaF_7-alkali halide systems, the experiments were conducted under different conditions. Finally, the influences of different K_2TaF_7 molten salt systems on the specific capacity of Ta powder were investigated.

2 PHASE DIAGRAM ANALYSIS

The species ratios were selected according to the phase diagrams of K_2TaF_7-alkali halide systems. In order to carry out the reaction thoroughly and obtain capacitor grade Ta powder with high quality and high specific capacity, several principles must be considered: (1) The M.P. of the molten salt must be as low as possible; (2) The M.P. of the reaction-ending system can not be too high, so as to ensure lower hold-up temperature; (3) The quantities of K_2TaF_7 in the burden ratio must be as large as possible for high yield.

2.1 K_2TaF_7-NaCl system

It is assumed that the total mole count of K_2TaF_7-NaCl system is 1, the mole count of K_2TaF_7 is x, and reaction (1) carries out thoroughly. Because the diluents do not participate in the reaction, the mole count of NaCl is $1-x$, and those of the reaction products KF and NaF are $2x$ and $5x$, respectively. There exist interactions among NaCl, KCl, NaF and KF[3], which are typical ion-pattern compounds and form a quarternary reciprocal system. The total mole count of each ion is as follows: Na^+ $(1+4x)$, K^+ $2x$, F^- $7x$ and Cl^- $(1-x)$. Thus, the values of Na^+/K^+ and F^-/Cl^- can be calculated:

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$k_1 = Na^+ / K^+ = (1 + 4x)/2x$ (2)

$k_2 = F^- / Cl^- = 7x/(1 - x)$ (3)

If the burden ratio is known, then the M. P. of the reaction-beginning system can be determined from Fig. 1. Meanwhile, k_1 and k_2 can be calculated with regard to equations (2) and (3). The M. P. of the reaction-ending system is determined from Fig. 2[5].

From equations (2) and (3), we can obtain equation(4):

$(2k_1 - 5) \times k_2 = 7 (k_1 > 2.5)$ (4)

If the M. P. of the reaction-ending system is known, the concrete position of the system

Fig. 2 Quarternary reciprocal diagram of KCl-NaCl-KF-NaF system

corresponding to Fig. 2 can be fixed, and the burden ratio of the reaction-beginning system can be determined as well. Based on the selective principles of the burden ratio and Figs. 1~ 2, the burden cases of K_2TaF_7-NaCl system[4] can be analyzed in detail. There are two eutectic points in K_2TaF_7-NaCl system(Fig. 1), namely, point *A*: K_2TaF_7/NaCl= 30/70(molar ratio), M. P. = 585 ℃; and point *B*: K_2TaF_7/NaCl= 78.5/21.5, M. P. = 672 ℃. According to equations (2) and (3), k_1 and k_2 of the reaction-ending system of point *A* are calculated to be 78.5/21.5 and 75/25 respectively, and its M. P. is found to be 870 ℃ from Fig. 2. The same processing applies to point *B*, getting k_1 = 72.5/27.5, k_2 = 96.1/3.9 and M. P. = 890 ℃.

In order to prevent the reactant interface from forming solid "crust of salt" which hinders reaction (1) going on, and ensure good fluidity of the melt, the reduction temperature must be controlled over the M. P. of the reaction-ending system. With regard to the dynamics of the reaction, the hold-up time at a certain temperature is just the period for the growth of Ta crystal nuclei. High temperature accelerates the crystal growth, coarses the Ta grains, and is not beneficial to prepare Ta powder with high specific capacity.

2.2 K_2TaF_7-KCl system

Assuming that the total mole count of K_2TaF_7-KCl system is 1, that of K_2TaF_7 is y, and reaction (1) carries on thoroughly, the total mole count of each ion is as follows: Na^+ $5y$, K^+ $(1+y)$, F^- $7y$ and Cl^- $(1-y)$. Thus:

$k_{12} = Na^+ / K^+ = 5y/(1+y)$ (5)

$k_{22} = F^- / Cl^- = 7y/(1-y)$ (6)

Eq. (7) can be obtained from Eqs. (5) and (6):

$2k_{12}k_{22} + 7k_{12} - 5k_{22} = 0$ (7)

If the burden ratio y is known, the M. P. of the reaction-beginning system can be found from Fig. 3[6], the burden composition of the reaction-ending system can be calculated from equations (5) and (6), and the M. P. of the corresponding system is known from Fig. 2.

On the contrary, if the M. P. of the reaction-ending system is certain, k_{12} and k_{22} corresponding to the M. P. of the system and in accordance with equation (7) can be known from Fig. 2. Therefore, the burden ratio of the reaction-beginning system is determined. Alternatively, both of the eutectic points of K_2TaF_7-KCl system are not the most proper burden ratio for producing Ta powder with high specific capacity.

Fig. 3 Binary diagram of K_2TaF_7-KCl system

2.3 K_2TaF_7-NaCl-KCl system

Assuming that the total mole count of K_2TaF_7-NaCl-KCl system is 1, that of K_2TaF_7 is u, and that of NaCl is v, then the total mole count of each ion is as follows: Na^+ $(5u + v)$, K^+ $(u - v + 1)$, F^- $7u$, Cl^- $(1 - u)$. Therefore,

$$k_{13} = Na^+ / K^+ = (5u + v)/(u - v + 1) \quad (8)$$

$$k_{23} = F^- / Cl^- = 7u/(1 - u) \quad (9)$$

The burden ratio of the reaction-beginning system corresponds to its M. P. from Fig. 4[7], and k_{13} and k_{23} of the reaction-ending system can be calculated from equations (8) and (9). Then the M. P. of the homologous system can be obtained from Fig. 2. On the other hand, if the M. P. of the reaction-ending system is known, k_{13} and k_{23} can be determined from Fig. 2 and the burden ratio of the reaction-beginning system can be deduced.

As mentioned above, to the reaction-ending system, the Na^+/K^+ ratio of K_2TaF_7-KCl system is larger (> 2.5) than that of K_2TaF_7-NaCl system(< 2.5), and that of K_2TaF_7-NaCl-KCl system is situated between them. The forms of equations (3), (6) and (9) are identical. So, if the mole count of K_2TaF_7 is certain, the F^-/Cl^- ratio is certain, and the hold-up temperature depends only on the quantity of NaCl or KCl.

Fig. 4 Ternary diagram of K_2TaF_7-NaCl-KCl system

3 K_2TaF_7 REDUCTION WITH SODIUM

According to phase diagram analysis and the principles for selecting burden ratio, several molten salt systems are listed in Table 1.

Table 1 Burden ratio of K_2TaF_7 system (mole per cent)

Samples	K_2TaF_7	NaCl	KCl
T-1	18.3	81.7	-
T-2	14.4	61.1	24.5
T-3	29.7	-	70.3
T-4	18.0	-	82.0
T-5	35.0	-	65.0

K_2TaF_7 was activated for 1 h at 250 ℃ and NaCl or KCl was calcined for 1 h at 450 ℃. Reactants were made up in the light of Table 1. The burden and liquid sodium(beyond theoretical quantity 15%) were mixed to form homogeneous paste. Then the reaction was in progress under a pressure of 100 kPa Ar at lower than 850 ℃. After a certain temperature was held up for 2 h, the reaction was over. The products were cooled, brought out, and washed by water and acids. Ta powder was heat-treated at 1 250 ℃ for 3 h and then examined.

The average size of Ta powder was examined. Its electric properties were tested in accordance with testing condition of 25V capacitor products (agglomeration at 1 600 ℃ for 30 min, power feed at 100 V for 2 h).

4 RESULTS AND DISCUSSION

The conditions of K_2TaF_7 reduction with sodium and the properties of Ta powder were listed in Table 2. It is shown that the M.P. of the reaction-beginning or reaction-ending system has relation to Na^+/K^+ ratio, as seen in Fig. 5. And the relation of the specific capacity of Ta powder to Na^+/K^+ ratio is plotted in Fig. 6.

Fig. 5 shows that the M.P. of the reaction-ending system tends to increase with Na^+/K^+ ratio. With the reaction carrying on, the amount of the product NaF with high M.P. increases. So the M.P. of the reaction-ending system of K_2TaF_7-NaCl becomes higher.

Fig. 6 shows that the specific capacity of Ta powder decreases with increasing Na^+/K^+ ratio, which has something to do with the M.P. of the reaction-ending system, namely, with increasing M.P. of the reaction-ending system, specific capacity of Ta powder reduces linearly.

Table 2 The reduction conditions and testing results

Sample No.	T-1	T-2	T-3	T-4	T-5
Na^+/K^+ ratio	4.73	2.50	1.14	0.76	1.30
F^-/Cl^- ratio	1.54	1.18	2.96	1.54	3.77
M.P. of reaction-beginning system / ℃	650	610	740	700	755
M.P. of reaction-ending system/ ℃	825	790	790	750	810
Hold-up temp. / ℃	850	800	800	760	850
FSSS size/ μm	3.01	2.72	2.39	1.70	2.80
Green density / $g\cdot cm^{-3}$	5.74	5.63	5.30	4.53	4.57
Shrinkage/ %	10.20	14.57	13.41	15.48	10.74
Specific capacitance / $\mu F\cdot V\cdot g^{-1}$	10160	13200	14820	17800	11788
Value K × 10^4 / $\mu(\mu F\cdot V)^{-1}$	6.84	3.06	3.45	4.35	4.70
Loss, tg δ	4.3	5.0	6.1	7.6	5.7

Fig. 6 Specific capacity of Ta powder *vs* Na^+/K^+

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