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THERMOCHEMISTRY OF ALKALI-METAL TITANATES

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ABSTRACT

The molar enthalpies of reaction at 970 K of sodium and potassium titanates have been determined by high-temperature solution calorimetry for the reactions: $mM_2TiO_3 + (n-m)TiO_2 = mM_2O\cdot nTiO_2$, where (m,n) = (1,1), (4,5), (1,2), (1,3) and (1,6) on M = Na, and (1,1), (2,3), (1,2), (1,4) and (1,6) on M = K. It has been indicated from the resultant data that $4Na_2O\cdot 5TiO_2$, $2K_2O\cdot 3TiO_2$ and $K_2O\cdot 2TiO_2$ might be stabilized at high temperatures by significant positive entropies . The enthalpies of formation at 970 K of these compounds have been derived from the combination of the present work with the literature data (ref.1,2). Melting points and degrees of hydrolysis of these compounds are reasonably correlated to their enthalpies of formation

INTRODUCTION

Titanates of alkali metals are increasingly important because of the possible utility of the compounds in the production of thermal insulators, ion-exchangers, and in other areas. These compounds are exhibited by a general formula, $mM_2O\cdot nTiO_2$, where M is an alkali metal. The literatures (ref.3-14) describe the preparations of the compounds of m:n = 2:1, 1:1, 4:5, 1:2, 1:4, 1:6 and 1:7 in Na_2O-TiO_2 system, and m:n = 2:1, 1:1, 2:3, 1:2, 1:6 and 1:8 in K_2O-TiO_2 system However, the phase relations in these systems are not established, because the literaure data available on the formation of these titanates are very contradictly.

It has been noticed that the thermochemical data available, which are necessary to predict the phase relations, are very scanty on these compounds, and the literature data are widely dispersed (ref. 1,2,6,15,16).

This work was devoted to provide the thermochemical data on sodium and potassium titanates, and to correlate them to the formation conditions, chemical or physical properties of the compounds. A high-temperature solution calorimetric method was employed with $3Na_2O\cdot 4MoO_3$ as the medium to measure heats of solution at 970 K.

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EXPERIMENTAL

Materials

Na_2CO_3, K_2CO_3 and TiO_2 of 99.99% purity were used on the preparations of samples for the calorimetric measurement. The starting mixtures with M_2CO_3:TiO_2 molar ratios from 1:1 to 1:6 were sintered for 30 h at 1225 K on Na_2CO_3-TiO_2 series, and at 1070 K on K_2CO_3-TiO_2 series. Sodium meta- and dititanate, which were not prepared from the mixtures of carbonate and oxide at temperatures above 970 K, were synthesized by heating the correponding stoichiometric mixtures of oxide and 4-N aqueous solution of sodium hydroxide for 10 h at 1080 K on the metatitanate, and 1020 K on the dititanate. During the heating periods there were two times of grindings and mixings. It was concluded from the analysis of the x-ray powder patterns of the sintered products that the following compounds were prepared: $Na_2O\cdot TiO_2$, $4Na_2O\cdot 5TiO_2$, $Na_2O\cdot 2TiO_2$, $Na_2O\cdot 3TiO_2$, $Na_2O\cdot 6TiO_2$, $K_2O\cdot TiO_2$, $2K_2O\cdot 3TiO_2$, $K_2O\cdot 2TiO_2$, $K_2O\cdot 4TiO_2$ and $K_2O\cdot 6TiO_2$; the x-ray patterns of these compounds basically agreed with the corresponding ASTM catalog data and ones reported by Batigin (ref. 8) on sodium meta- and dititanate, and by Belyaev et al. (ref.6) on $2K_2O\cdot 3TiO_2$. The thermal behaviors of the products were examined by TG-DTA.

Calorimetry

A Calvet twin microcalorimeter available to 1250 K was constructed in cooperation with Tokyo Riko Co.. Fig.1(A) shows the central part of this apparatus which was desighned on the basis of the calorimeters constructed by Kleppa (ref.17,18). Two cylindrical calorimeter units were located in two wells of a sintered alumina constant-temperature jacket, 20 cm high and 20 cm in diameter. Each thermopile was composed from 180 junctions of Platinel thermocouple of 0.5 mm in diameter. The calorimeter unit was built up from a stack of fifteen identical element, in where twelve thermocouple junctions were radially arranged (Fig. 1(B)). The furnaces, which were separated in three zones and wound with Kantal resistance wires on a alumina outer jacket of 30 cm in diameter, were heated by three constant DC supplies. The output of the thermopile connected in opposition to each other was fed to a microcomputer through a degital voltmeter after amplifing. The sample assembly used in the present work is shown in Fig. 1(C). The calibration constant of the calorimeter obtained by Pt-drop method was 13.5±0.15 $J\cdot mV^{-1}$ min^{-1} at 970±2 K. The experiments were performed at this temperature . The solvent $3Na_2O\cdot 4MoO_3$ was prepared from WO_3 and Na_2WO_4 of 99.9%

purity. In each solution experiment a 40-60 mg of sample was dissolved in 30 g of melt. The solvent was renewed after three experiments. The stirring heat effect of the order of 0.05±0.01 J in each solution experiment was corrected.

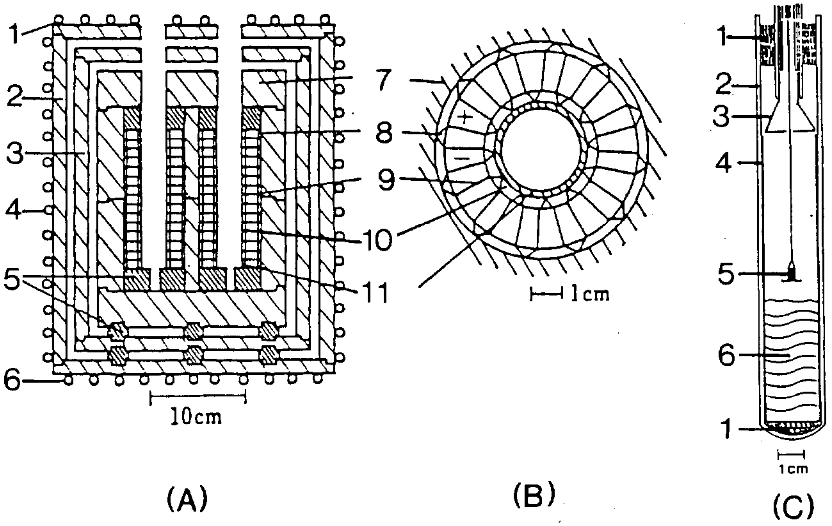

Fig. 1. Twin differential heat flux calorimeter
(A) Central part of the calorimeter; (B) A thermopile element; 1: Top heater; 2 and 4: Main heater; 3: Thermal screen; 5: Mullite spacer; 6: Bottom heater; 7: Isothermal jacket; 8 and 10: Alumina ring; 11: Cell holder; Slashed part (coarse): Sintered alumina; Slashed part (fine): Sintered mullite, (C) Sample assemble; 1: Silica wool; 2: Quartz liner; 3: Platinum shield; 4: Platinum crucible; 5: Platinum sample cup; 6: Solvent

RESULT AND DISCUSSION

In Table 1 are presented the results of solution experiments on the ten titanate compounds mentioned before and TiO_2 (rutile). ΔH_{sol} of Na_2O and K_2O were not measured because these substaces are not stable at 970 K in air. $\Delta H_{sol}/(m+n)$ are plotted to $n/(m+n)$ in Fig.1. ΔH_r(970K) of the reactions (1) were derived on the basis of these enthalpy values of solution; $M_2O{\cdot}TiO_2$-TiO_2 systems contain all important compounds for utility (ref.19).

$$mM_2TiO_3 + (n-m)TiO_2 = mM_2O{\cdot}nTiO_2 \qquad (1)$$

The enthalpies of reaction ΔH_r(970K) are listed in Table 2, and ΔH_r(970K)/(m+n) in the present work are plotted with those derived from thermochemical tables given by Bennington and Brown (ref.15), and from the compilation by Barin, Knacke and Kubaschewski (ref.1), in Fig.2. Table 2 and Fig. 2 indicate that ΔH_r(970K) are negative values for all compounds prepared in this work, though ΔH_r(970K)

TABLE 1

Enthalpies of solution of several sodium and potassium titanates and rutile in $3Na_2O\cdot4MoO_3$ melt at 970 K, and enthalpy changes associated with reactions (1)

Substances	$\Delta H_{sol}(970K)/kJ\cdot mol^{-1}$		$\Delta H_r(970K)/kJ\cdot mol^{-1}$	
	M=Na	M=K	M=Na	M=K
TiO_2	9.42±0.32[a]		0	
$M_2O\cdot6TiO_2$	34.03±1.33	74.93±0.65	-51.1±2.1[b]	-130.3±1.6
$M_2O\cdot4TiO_2$	-	16.31±1.13	-	-90.6±2.0
$M_2O\cdot3TiO_2$	-17.35±1.73	-	-27.9±2.4	-
$M_2O\cdot2TiO_2$	-34.70±1.08	-85.24±0.82	-20.1±1.8	-7.8±1.5
$2M_2O\cdot3TiO_2$	-	-193.4 ±4.3	-	-2.2±5.0
$4M_2O\cdot5TiO_2$	-246.5 ±3.1	-	-0.8±6.6	-
$M_2O\cdot TiO_2$	-64.18±1.45	-102.5 ±1.3	0	0

[a] uncertainties are standard deviations (σ) of the mean of 3-5 run

[b] uncertainties $\sigma_r = \sqrt{m^2\sigma_1^2 + (n-m)^2\sigma_2^2 + \sigma_0^2}$

TABLE 2

Enthalpies of formation of several sodium and potassium titanate at 970 K

Substance	$\Delta H_f(970K)/kJ\cdot mol^{-1}$	
	M=Na	M=K
$M_2O\cdot6TiO_2$	-6020	-6053
$M_2O\cdot4TiO_2$	-	-4213
$M_2O\cdot3TiO_2$	-3298[a]	
$M_2O\cdot2TiO_2$	-2390	-2331
$2M_2O\cdot3TiO_2$	-	-3748
$4M_2O\cdot5TiO_2$	-6779	-
$M_2O\cdot TiO_2$	-1470	-1423[b]

[a] Barin, Knacke and Kubaschewski (ref.1)

[b] Kutolin and Sergeeva (ref.2)

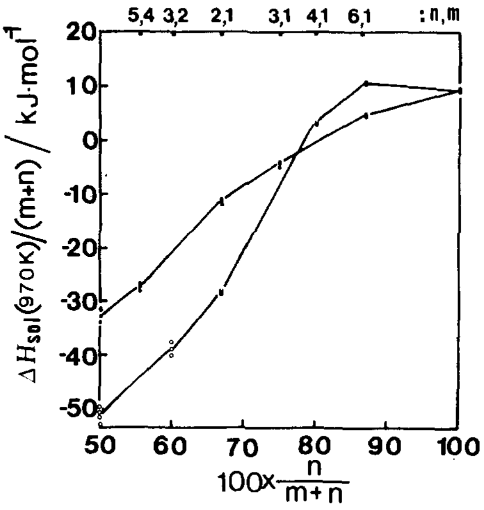

Fig. 2. Normalized Enthalpies of Solution at 970K
●: Sodium titanates, ○: Potassium titanates

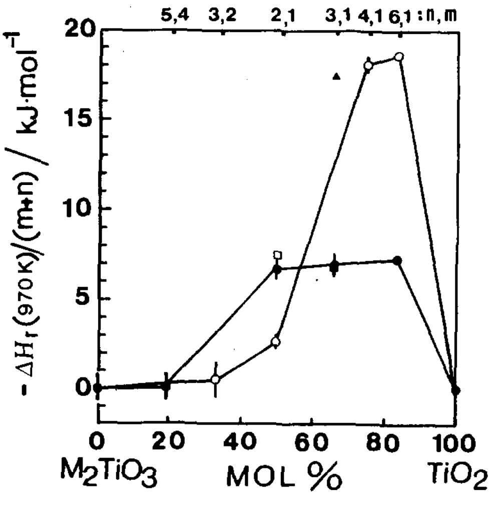

Fig. 3. Normalized Enthalpies of Reaction at 970 K
●: Sodium titanates , ○: Potassium titanates, □: Barlin et al. (ref.1), ▲: Bennington & Brown (ref.15)

for $4Na_2O\cdot5TiO_2$ and $2K_2O\cdot3TiO_2$ are not negative over the experimental uncertainties. On the other hand, the enthalpy changes associated with the reaction (2) and (3) are found to be positive values of 19.3±5.7 and 22.3±1.6 $kJ\cdot mol^{-1}$, respectively.

$$3Na_2TiO_3 + Na_2O\cdot2TiO_2 = 4Na_2O\cdot5TiO_2 \qquad (2)$$

$$(2/3)K_2TiO_3 + (1/3)\cdot K_2O\cdot4TiO_2 = K_2O\cdot2TiO_2 \qquad (3)$$

Thus, $4Na_2O\cdot5TiO_2$ and $K_2O\cdot2\ TiO_2$ seem to be less stable than the phase combinations indicated in the reaction (2) and (3). However, the estimate are not agreement with the prediction based on their synthetic conditions; both compounds are known to be easily formed at wide temperature ranges up to their melting points. These facts suggest the significant positive entropies of reaction must be considered on these reactions.

As shown in Fig. 3, for reaction (1), our ΔH_r(970K) are consistent with the data by Barin et al. within experimental uncertainties, but markedly deviate from the data determined by Bennington and Brown using HF solution calorimetry. Bacause of the good consistency with our data, the enthalpy value of formation of $Na_2O\cdot3\ TiO_2$ by Barlin et al. was used to calculate enthalpies of formation of the other sodium titanates. The results are given in Table 2 and Fig. 4. The remarkable discrepancy between both literature data on H_f(970K) is attributed to the different heat capacity data used. In addition, it may be pointed out that our sodium metatitanate sample decomposed to a mixture with $4Na_2O\cdot5TiO_2$ at the preparation temperatures (1183-1370 K) reported by Bennington and Brown. To Calculate ΔH_f(970K) of potassium titanates, ΔG_f(970K) of $K_2O\cdot TiO_2$ by Kutolin and Sergeeva (ref.2) was used, where its heat capacity was estimated from the data of sodium trititanate (ref.1). It is shown in Fig.4 that ΔH_f(970K) of potassium titanates negatively exceed those of sodium titanates in a Ti-rich region, but the increasing alkali content brings about the reverce change.

In Fig. 5 and 6 are plotted the correlations of ΔH_f(970K) to melting points and degrees of hydrolysis of the titanate compounds , respectively. It is concluded that the linear relations have been approximately established among those.

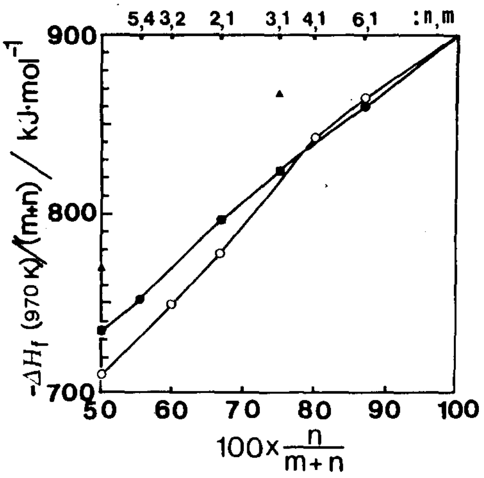

Fig. 4. Normalized Enthalpies of Formation at 970 K
●: Sodium titanates, O: Potassium titanates, ■: Overlap on ● of sodium tri-, di- and metatitanate, Barin et al., ▲: Bennington & Brown

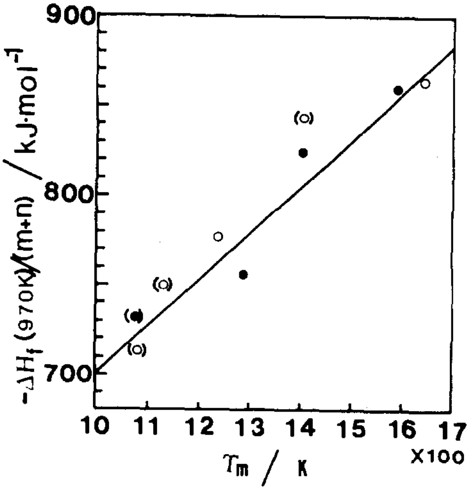

Fig. 5. ΔH_f - T_m Correlation
●: Sodium titanates, O: Potassium titanates, (): Incongruent melting points

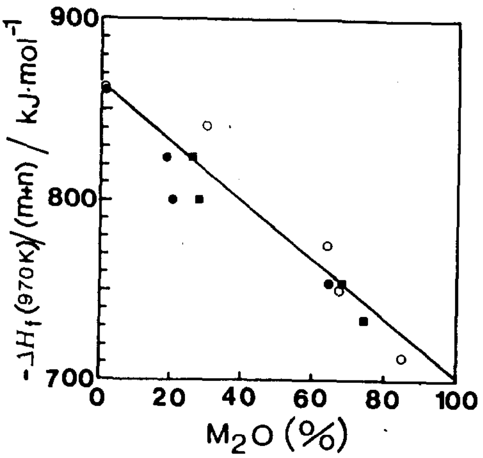

Fig. 6. ΔH_f - M_2O Correlation
M_2O: Extraction ratio, ●: Sodium titanates (ref.6), ■: Sodium titanates (ref.8), O: Potassium titanates (ref.12)

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