REACTION OF STRONTIUM SULFATE WITH ANATASE AND RUTILE BELOW AND ABOVE THE PHASE TRANSITION TEMPERATURE OF STRONTIUM SULFATE

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ABSTRACT

The solid-state reaction of strontium sulfate with anatase and rutile was examined by isothermal and non-isothermal TGA/DTA and X-ray diffraction. The endothermic peak due to the reversible phase transition of $SrSO_4$ was observed by DTA in the vicinity of the endothermic peak due to the reaction. The product was only $SrTiO_3$ in all cases. The reaction mechanism was described by the Jander model. The rate constant for anatase was about twice as large as that for rutile. The relation between $\ln k_J$ and T^{-1} for anatase and rutile was discontinuous being linear either side of the phase transition temperature of $SrSO_4$. The rate constant just above the transition temperature was enhanced 1.5 times with respect to that just below the temperature. The activation energy for the reaction of strontium sulfate with rutile was 354 and 435 kJ mol^{-1} in the higher and lower temperature regions respectively. In the reaction with anatase, the phase transition of anatase to rutile was also observed in about 30% of the fraction reacted at any temperature, and the rate constant was scattered from the $\ln k_J$ vs. T^{-1} curve, especially at high temperatures.

INTRODUCTION

The chemical reactivity of starting materials can be determined quantitatively if kinetic data are available, otherwise the initial temperature of the reaction in a thermogravimetric study can be used. In order to investigate the immobilization of high-level radioactive waste in the form of titanate-based ceramics under mild conditions, we have studied the reactivity of starting materials and the kinetics of formation of alkaline earth metal titanates by the reaction of some salts of alkaline earth metals with anatase, rutile and the hydrate form of titanium dioxide [1–3]. Studies on the

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formation of the titanates have been performed by many workers, but there are no results reported on the reaction of strontium sulfate with titanium dioxide. In this paper, the kinetics for the reaction of strontium sulfate with anatase and rutile were studied for comparison with those of the other reactions. In the course of the experiments, it was found that the rate constant was enhanced above the phase transition temperature of $SrSO_4$, 1161°C. It is reported that the crystal structure of $SrSO_4$ is changed from the orthorhombic to the cubic at 1156 ± 5°C [4].

EXPERIMENTAL PROCEDURE

Strontium sulfate provided by the Kanto Chemical Co., and anatase and rutile, which were provided by the Wako Chemical Co., were used as starting materials. The average particle sizes of the anatase and rutile, which were determined by scanning electron microscopy (SEM), were 0.18 ± 0.02 and 0.26 ± 0.03 μm, respectively. The shape of these particles was nearly spherical. Strontium sulfate and anatase or rutile were thoroughly ground and mixed in an equimolar ratio in a sintered high-purity alumina mortar and compacted at 1.5×10^3 kg cm^{-2} into cylindrical pellets, 7 mm in diameter and 3.5 mm in height. According to SEM observation, the particle sizes of the strontium sulfate after grinding were about 4.7 μm, although the sizes were not always uniform. The particles of anatase or rutile were seen to cover adhesively the particles of strontium sulfate. The weight of the pellets used was 300 mg.

The reaction kinetics experiments were performed isothermally with a TG–DTA apparatus (Shinku-Riko Co, type TGD-5000). The apparatus consisted of an electrobalance, a thermocouple for measuring the sample temperature, a reference thermocouple for DTA, and an IR image furnace. A platinum sample holder, 8 mm in diameter and 10 mm in height, was attached to one end of the arm of the balance. A sheath for the thermo-couple, 1 mm in diameter and projecting 5 mm up into the sample holder, was welded to the bottom center of the holder. The depth remaining for the pellet was 5 mm.

Most isothermal experiments were carried out using the samples in pellet form. After the pellet was loaded in the holder, air was allowed to flow at 100 cm^3 min^{-1}. The linear air velocity at the wall of the sample holder was calculated to be 30 cm min^{-1} at room temperature. The sample was heated at 100°C min^{-1} to the desired temperature and kept at that temperature for 8 h or less. For non-isothermal experiments, a powder specimen was used and a heating rate of 5°C min^{-1} was chosen.

X-ray diffraction (XRD) analysis of the powder specimens was obtained on a Rigaku Denki Co., type Rad-1A, diffractometer using Cu Kα radiation monochromatized with a bent graphite crystal.

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTA curves obtained on heating equimolar mixtures of strontium sulfate and anatase or rutile at a heating rate of $5\,^\circ$C min^{-1} in air flowing at 100 cm^3 min^{-1}. Also shown is the DTA curve on heating and cooling strontium sulfate. The TG and DTA curves were simultaneously obtained. About 200 mg of the sample powder was used.

For strontium sulfate, the DTA curve showed an endothermic peak with the extrapolated onset temperature of $1161\,^\circ$C on heating and an exothermic peak at $1135\,^\circ$C on cooling. This peak is due to the phase transition from the orthorhombic to the cubic structure. Thermal decomposition of strontium sulfate was not observed below $1300\,^\circ$C.

The reaction of strontium sulfate with anatase and rutile occurred at about 920 and $935\,^\circ$C respectively. In the reaction with anatase, the anatase was transformed into rutile at $1310\,^\circ$C. This phase change was confirmed by XRD analysis of the sample raised to various temperatures using the same TG–DTA apparatus. The phase transition of anatase to rutile could not be detected by DTA. When anatase was heated on its own at $5\,^\circ$C min^{-1} in flowing air, it was completely changed into rutile by $1230\,^\circ$C, which was
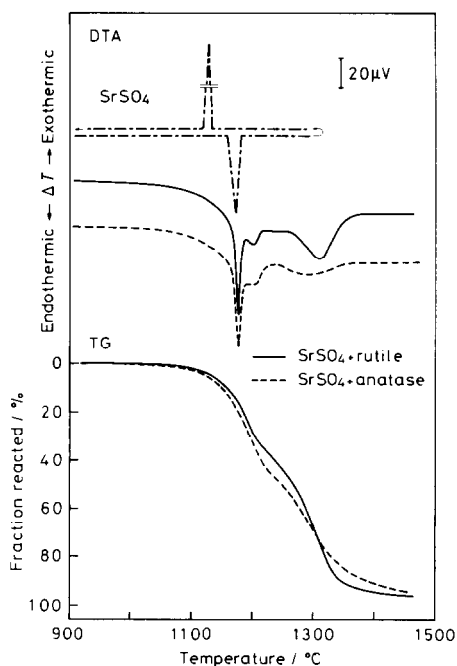

Fig. 1. TG and DTA curves obtained simultaneously for the reaction of strontium sulfate with anatase and rutile at a heating rate of $5\,^\circ$C min^{-1} in a 100 cm^3 min^{-1} air flow, and DTA curve of strontium sulfate at a heating and cooling rate of $5\,^\circ$C min^{-1}.

about 80 °C lower than the transition temperature obtained for the mixture of the $SrSO_4$ and anatase. The temperature difference between these two conditions is therefore indicative of a shift of the anatase–rutile transition toward higher temperature in the presence of impurities such as sulfate ions [5]. The weight loss curve for the reaction of $SrSO_4$ with anatase, which is shown as the fraction reacted in Fig. 1, lies at slightly lower temperature than that for rutile. DTA curves for the reactions of strontium sulfate with anatase and rutile consist of one sharp and two broad endothermic peaks. The first peak is due to the phase transformation of strontium sulfate, and the latter two peaks are due to the reaction of strontium sulfate with TiO_2. The latter two peaks correspond to the two steps seen on the TG curve. According to the XRD analysis for the quenched sample, only $SrTiO_3$ was formed during the reaction.

The initial temperature of the reaction of strontium sulfate with titanium dioxide, measured in this work, was higher than the temperatures for the reaction of other strontium salts (carbonate, hydroxide and nitrate) with titanium dioxide, previously reported [1]. Figure 2 shows the initial temperatures of reaction on the standard Gibbs energy changes vs. temperature curves for the formation of $SrTiO_3$. The Gibbs energies were calculated by
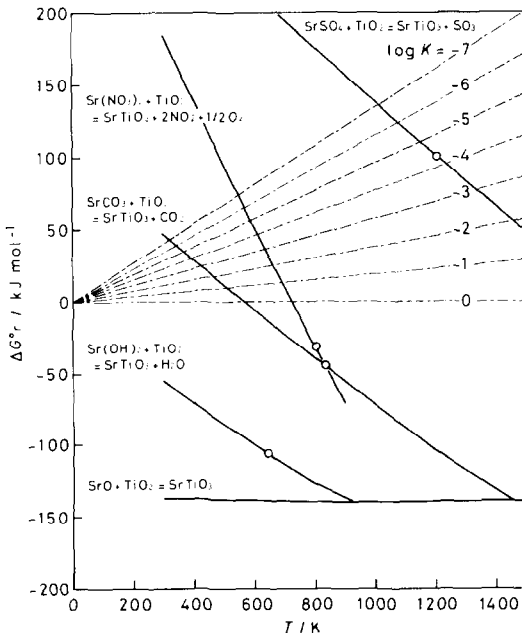

Fig. 2. The initial reaction temperatures [1] in flowing air at 5 °C min^{-1} plotted on the curves of the standard Gibbs energy changes for the formation of $SrTiO_3$ by the reaction of strontium carbonate, hydroxide, nitrate and sulfate with rutile, where the value for $SrSO_4$ was obtained in the present work.

using the "thermodynamics" data base [6]. The Gibbs energy for $SrTiO_3$ formation by the reaction with anatase is 5 kJ mol^{-1} more negative than that with rutile. In the figure, the open circles represent the experimentally obtained initial temperatures of the $SrTiO_3$ formation reactions obtained experimentally. It is seen that the initial temperatures, which reflect the reactivity of the starting materials, roughly correlate with their standard Gibbs energy changes for the formation of $SrTiO_3$: that is, the more negative the Gibbs energy change for the reaction, the higher the reactivity of the starting material. Thus, it is known that the reaction of $SrSO_4$ with TiO_2 occurs at much higher temperature than the other reactions using strontium carbonate, hydroxide and nitrate.

Before studying the isothermal reaction kinetics, the change in sample temperature was examined in the vicinity of the strontium sulfate phase transition temperature, 1161°C, in the reaction of strontium sulfate with rutile. In order to measure the interior temperature of the sample, a powder specimen was used. The 300 mg sample was heated at 100°C min^{-1} and then maintained at 1157 and 1163°C. The results are shown in Figs. 3 (a) and (b) respectively. The heating curve, the temperature difference between the sample and the alumina reference material, and the $[1 - (1 - \alpha)^{1/3}]^2$ vs. time curve, the so-called Jander plot are shown. In the DTA curve of Fig. 3 (a), after the dehydration has finished at 400°C and the sample temperature reaches 1157°C an endothermic peak due to the reaction is observed. In Fig. 3 (b), the endothermic peak due to the strontium sulfate phase transition occurs just before the sample reaches 1163°C, where the second endothermic peak due to the reaction is observed.

Figure 4 shows the degree of conversion α vs. time curves for the reaction of strontium sulfate with rutile for pellet samples. The reacted fraction curves flatten out at fractions increasing with temperature. The reacted fraction failed to reach 100% even when the sample was kept at temperatures as high as 1250°C for a long time. For anatase, similar curves were also obtained. The product consisted of $SrTiO_3$ and the starting materials at all temperatures. The conversion calculated on the basis of weight loss was in good agreement with that obtained from XRD.

The reaction mechanism was determined by fitting the data to the following models: the phase boundary reaction control model, $k_C t = 1 - (1 - \alpha)^{1/3}$; the Jander model [7], which is the approximately parabolic rate law as expressed by Eq. (1); the Dunwald and Wagner model [8], $k_{DW} t = -\ln\{\pi(1 - \alpha)/6\}$, and the Ginstring and Brounstein model [9], $k_{GB} t = 1 - 2\alpha/3 - (1 - \alpha)^{2/3}$. Of these equations, the Jander model gave the best fit to the observed relation between fraction reacted and time. The Jander equation is given as:

$$k_J t = \left\{1 - (1 - \alpha)^{1/3}\right\}^2 \tag{1}$$

where k_J is the reaction rate constant and t is the time. Figure 5 shows the

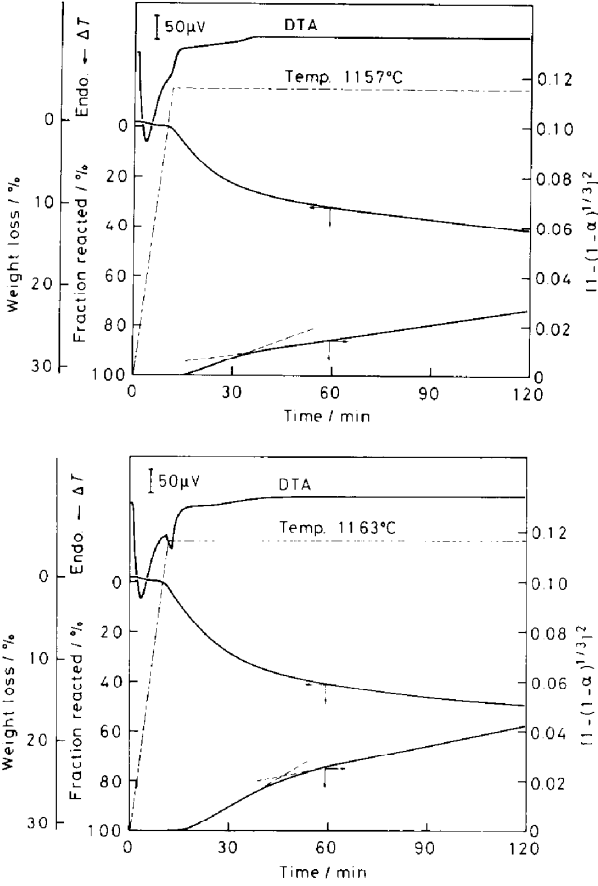Fig. 3. Weight loss, differential temperature between the sample and the reference alumina, the sample temperature and $[1-(1-\alpha)^{1/3}]^2$ for powder specimens at 1157 and 1163°C for the reaction of strontium sulfate with rutile.
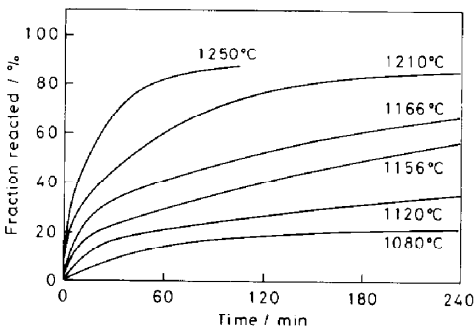

Fig. 4. Relationship between reacted fraction and time for the cylindrical pellets for the reaction of strontium sulfate with rutile.

$\{1 - (1 - \alpha)^{1/3}\}^2$ vs. time curves calculated from the data of Fig. 4. The gradient of the curve gives the rate constant, k_J. Generally, the Jander model gives a satisfactory reaction rate constant for small values of the reacted fraction. The accuracy of the model has been discussed, in terms of the approximations involved, elsewhere [3].

For Fig. 5, each curve is seen to deviate from linearity at a reacted fraction of between 20 and 40, although the value of the fraction reacted is close to the limit for applying the Jander model. Two rate constants were obtained from each curve. The time at which the curve deviated from linearity decreased exponentially with the increase in the reaction temperature, for example from 90 min at 1090°C through 25 min at 1160°C to 7 min at 1220°C for rutile and from 150 min at 1090°C through 35 min at 1160°C to 8 min at 1220°C for anatase. To try to understand why the curves should depart from linearity, mixtures of $SrSO_4$ and rutile were heated for 15, 90 and 350 min at 1166°C and then examined by XRD. The first heating time was located before the departure from linearity and the second and third ones after. The fraction reacted in these samples was 24, 44 and 73% respectively. The XRD patterns of these samples showed them to be only a mixture of $SrTiO_3$ and the starting materials. The bulk density of the product was observed to increase as the temperature was raised. The reason for the non-linear behavior was not clear. It may be that reaction in the period before the deviation is between small particles of the starting materials and the reaction after the deviation proceeds between larger particles which have being coarsened or sintered. The same reaction behavior was also found for anatase.

The temperature dependence of the reaction rate constant is given by the expression,

$$k_J = C \exp(-Q/RT) \tag{2}$$

where C is some constant, Q the activation energy, R the gas constant and
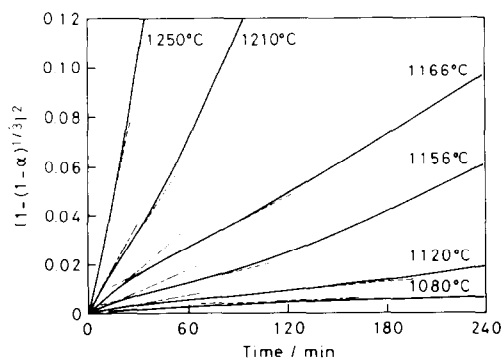

Fig. 5. Relation between $[1 - (1 - \alpha)^{1/3}]^2$ and time for the results shown in Fig. 4.

T the absolute temperature. Figure 6 shows the relation between rate constant and reciprocal absolute temperature for the reaction of strontium sulfate with rutile; open circles show the rate constant obtained before the deviation from linearity, and closed circles show the rate after deviation. The relationship between $\ln k_J$ and T^{-1} is linear but discontinuous at $1161°C$, where the gap width is about 0.4 in $\ln k$. The activation energies have been calculated by a least-squares method to be 354.1 ± 2.5 and 434.7 ± 4.6 kJ mol^{-1} respectively either side of the discontinuity. The rate after the deviation became smaller than the rate before: the activation energies in the higher and lower temperature regions are 484.4 ± 2.3 and 440.3 ± 4.0 kJ mol^{-1} respectively.

The discontinuity temperature, $1161°C$, of the $\ln k_J$ vs. T^{-1} curve is the same as the phase transition temperature of strontium sulfate obtained in this work. This means that the reaction rate constant was enhanced above the phase transition temperature. The phenomenon that a reaction rate can be affected by a phase transition has been observed by Hedvall [10]. As far as we can see in the given examples, the effect proposed by him occurs only at or just above a phase transition temperature. For the examples, the relation between the rate constant and the temperature is not apparent. Hedvall has stated [10], that this effect occurs during the relaxation of the newly-formed and distorted lattice caused by the phase transition to the stable lattice. The effect found in the present study, however, is though to come from the difference in the reactivity between the two crystal structures, rhombohedral and cubic of $SrSO_4$ in the higher and lower temperature
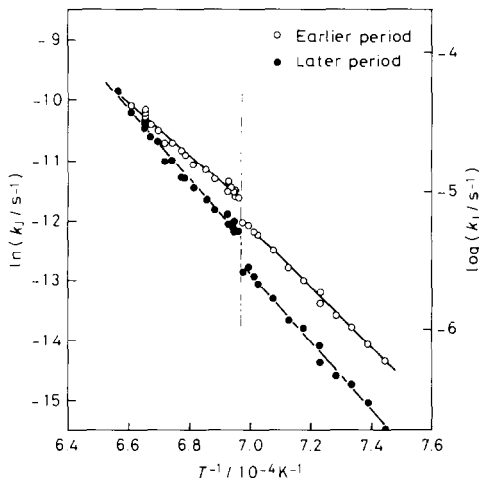

Fig. 6. Relation between $\ln k_J$ and T^{-1} for the reaction of strontium sulfate with rutile. Open and filled circles show the reaction rate constants at the earlier and later periods, respectively.
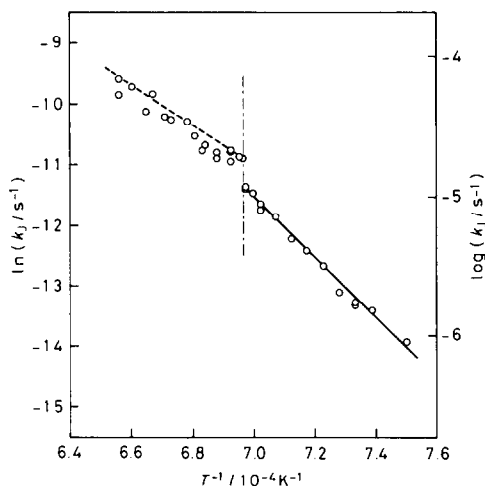
Fig. 7. Relation between ln k_J and T^{-1} for the reaction of strontium sulfate with anatase.

regions respectively. Even if distortion at the lattice is caused, the relaxation will probably finish soon after the phase transition occurs, because of the high temperatures at which the reaction proceeds.

Figure 7 shows the relation between ln k_J and T^{-1} for the reaction of strontium sulfate with anatase. In the figure, it is seen that the rate constant is also enhanced above 1161°C as with the reaction with rutile. The rate constant values for anatase, however, was much more scattered than those for rutile, especially at higher temperatures. The anatase was transformed into rutile during the reaction, but the time required for the transition was not always constant at any temperature. The phase transition finished within 80 and 20 min at 1120 and 1157°C. The conversion to $SrTiO_3$ at that time was around 30% in both cases. Thus, it is deduced that the scatter of the rate constant on the ln $k-T^{-1}$ curve results from the difference in reactivity between anatase and the newly-formed rutile, following the phase transition of anatase during the reaction. It is known that the activation energy of the reaction of strontium sulfate with anatase gives not the real, but the apparent value. If the activation energy is calculated, the value in the higher temperature region, which is obtained by plotting the highest rate constants at any temperature, is 279 kJ mol^{-1}, and that in the lower temperature region is 416.2 $\pm$ 3.1 kJ mol^{-1}.

CONCLUDING REMARKS

The formation of strontium titanate by the solid-state reaction of strontium sulfate with anatase and rutile was examined by TG–DTA and XRD. The

endothermic peak due to the phase transition of $SrSO_4$ appeared before the endothermic peak due to the reaction in the DTA. The initial temperature for the reaction of $SrSO_4$ with TiO_2 obtained by TG was much higher than those for the other reactions of $SrCO_3$, $Sr(OH)_2$ and $Sr(NO_3)_2$ with TiO_2 reported elsewhere. It was shown that the initial temperatures was related to the Gibbs free energy change for the titanate formation reactions.

The kinetics of the reaction of $SrSO_4$ with anatase and rutile in air was described by the Jander model for diffusion of reactant through a product layer. The Jander relation deviated from linearity at 20–40% of the fraction reacted for both rutile and anatase. It was deduced that the deviation was caused by the coarsening of particles of the starting materials and/or the product during the reaction rather than a change in mechanism.

The $\ln k$ vs. T^{-1} relation for anatase and rutile gave two straight lines with a discontinuity at 1161°C at which temperature the phase transition of $SrSO_4$ had occurred. The rate constant just above the transition temperature was about 1.5 times as high as that just below the temperature. The difference in the rate constants above and below the transition temperature was deduced to be due to the difference in the chemical reactivity of $SrSO_4$ with the crystal structures before and after the phase transition.

For the reaction of strontium sulfate with anatase, the phase transition of anatase occurred during the reaction and the time required for completing the phase change was not always constant at any temperature. Scatter in the values of the rate constant was seen in the $\ln k_J$ vs. T^{-1} relation, especially at high temperatures. It was deduced that the scatter came from the difference in the reactivity between anatase and the newly-formed rutile, resulting from the anatase phase transition.

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