Kinetics of Formation of $SrWO_4$ in the Solid State Reaction Between WO_3 and $SrCO_3$

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The solid state reaction $WO_3 + SrCO_3 \rightarrow SrWO_4 + CO_2$ was studied with the reactants in form both of separate pellets and of powder mixtures.

As for pellets, by an application of Wagner's method it was possible to state that the governing process is the cation counterdiffusion involving W^{6+} and Sr^{2+}.

Thermogravimetric measurements in the temperature range $663° - 755\ °C$ on equimolar powder mixtures and with $SrCO_3$ in a specially prepared spherulitic form were interpreted using Dünwald-Wagner's equation.

As a part of a research program on solid state reactions [1], the present paper reports results on the kinetics and transport mechanism of the reaction

$$WO_3 + SrCO_3 \rightarrow SrWO_4 + CO_2 .$$

As recently observed [2], little attention has been given so far to reactions of this kind, in which one of the products is in the gaseous state, particularly for what concerns the governing mechanism.

The kinetic process was investigated with the reactants in the form both of separate pellets and of powder mixtures. As for the latter the thermogravimetric isothermal method was applied to equimolar reacting mixtures in the temperature range $663° - 755\ °C$.

Since the adopted kinetic equation requires a model consisting of uniform radius spheres of one reactant surrounded by smaller particles of the other reactant [3], particular care was devoted to the preparation of mixtures of known form and size of the particles.

In order to characterize the mechanism, Wagner's method [4] was employed.

Experimental

a) Apparatus

TG and isothermal curves on powder mixtures were recorded by a Du Pont "950 Thermogravimetric Analyzer" joined with a "900 Differential Thermal Analyzer" (sample weight ~ 20 mg; sensitivity 2.5 inch/mg; heating rate (for TG) $3°$/min).

For measurements on pellets a tubular horizontal Heraeus furnace (controlled to $\pm 1\ °C$) was employed: a good contact between the pellets (inside a quartz tube) was accomplished by two platinum disks spring-pressed against the outer surfaces of the pellets through two nickel rods.

For X-ray diffraction experiments a Philips equipment was used.

b) Materials and Procedure

WO_3: X-ray analysis on a Koch-Light 99.9% product, prefired at $800\ °C$, and ball-milled to an average size of the granules of $\sim 1\ \mu m$, gave values of interplanar spacing which agreed with those by Gebert and Ackermann [5] for stoichiometric WO_3. A weight loss due to WO_3 sublimation was detected by TG starting from $800\ °C$. Pellets 8 mm wide and ~ 1.5 mm thick were obtained by pressing ~ 400 mg of the powder at 10^3 kg/cm², and then sintered by heating 5 h at $800\ °C$.

$SrCO_3$ and $SrWO_4$ pellets of the same size were also prepared at 10^3 kg/cm².

$SrCO_3$: Spherulitic $SrCO_3$ for TG and isothermal measurements was prepared by precipitation from solutions of Na_2CO_3 and $SrCl_2$ (both C. Erba RP) in the presence of gelatine as suggested by Morse and Donnay [6], prefired at $750\ °C$ for 5 h, and finally classified by sieving and by repeated sedimentation from an acetone suspension, thus isolating a fraction in which 80% of spherules was $10 \pm 2\ \mu m$ in diameter. A thermal decomposition of this sample was detectable by TG only from $800\ °C$ upwards: any weight loss revealed during the kinetic study (temperature range: $663 - 755\ °C$) may be therefore attributed to CO_2 development in the reaction course.

A Koch-Light 99.999% product (average granule size: ~ 1 μm) was used for the preparation of ~ 200 mg pellets, subsequently sintered (5 h at 700 °C).

SrWO₄: A ROC/RIC 99.9% product was employed for ~ 300 mg pellets, also sintered before use (5 h at 750 °C).

Mixtures WO₃ – SrCO₃ (1 : 1): WO₃ (1 μm) and SrCO₃ (10 μm) were mixed by suspending both powders in acetone and then evaporating with stirring to dryness; thus avoiding the breaking of the rather brittle spherulites.

Results and Discussion

Measurements on pellets

Since preliminary X-ray analysis showed that in WO₃ | SrCO₃ couples held ~ 50 h at $700° - 800$ °C the Sr₃WO₆ compound[7] formation was detectable only when $T > 760$ °C, kinetic measurements were performed in the range $700° - 750$ °C. The reacted couples were easily separable into two distinct pieces: X-ray analysis of the surfaces showed that the produced SrWO₄ adhered on the SrCO₃ pellet only. Furtherly, the latter, when cutted parallel to the diffusion direction and subjected to microscopic observation, did not reveal a distinct separation line between the layers of the formed SrWO₄ and SrCO₃. This prevented to study the reaction kinetics by measuring the thickness of the product layer.

To characterize the transport mechanism of the diffusing species, according to Wagner[4] two pellets of the product were sandwiched between those of the reactants and the weight changes due to reaction were evaluated.

In the present case, the sequence

$$WO_3 \,|\, SrWO_4\,(I) \,|\, SrWO_4\,(II) \,|\, SrCO_3$$

was heated for 240 h at 740 °C. The pellets weight changes (mg) of three runs, in all of which it was possible to separate the pellets without losses, are reported in Table 1, where the values in brackets are calculated from the amount of SrWO₄ formed.

Table 1. Weight changes (mg) of the pellets (240 h, 740 °C).

WO₃	SrWO₄ (I)	SrWO₄ (II)	SrCO₃
−4.2 (−1.9)	+1.8	+1.0	−2.5 (−1.2)
−4.1 (−1.5)	+1.5	+0.6	−2.0 (−0.9)
−3.8 (−1.8)	+1.7	+0.9	−2.3 (−1.1)

After separation, the contact surfaces of both pellets (I) and (II) with the reactants, as well as those of the reactants themselves, revealed by X-ray analysis their typical reflections only.

In all three runs the weight losses of WO₃ and SrCO₃ were larger than the calculated ones, the differences agreeing with the losses occurring when WO₃ and SrCO₃ pellets were heated separately for the same time and at the same temperature.

From the weight increase, occurring in both SrWO₄ pellets, it is apparent that the process-governing mechanism is the cation counterdiffusion through the product layer.

Thence it can be deduced that the following reactions:

$$3\,Sr^{2+} + 4\,WO_3 \rightarrow 3\,SrWO_4 + W^{6+}$$
$$W^{6+} + 4\,SrCO_3 \rightarrow SrWO_4 + 3\,Sr^{2+} + 4\,CO_2$$
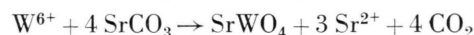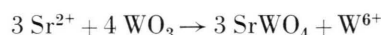
respectively occurr at the interfacies WO₃ | SrWO₄ (I) and SrWO₄ (II) | SrCO₃.

This reaction scheme requires that the ratio of the weight increases for pellets (I) and (II) should be 3. From the data in Table 1, a value of the ratio 2.1 ± 0.3 is evaluated, which can be considered satisfactory if allowance is made of the fact that both WO₃ sublimation[8] and SrCO₃ decomposition are already effective at 740 °C.

Measurements on powders

Preliminary TG measurements on the 1 : 1 molar mixture (reasonably conforming to the model already described, since the surface of a sphere of 10 μm diameter can be completely coated by 440 spheres of 1 μm, whereas in the present case the ratio of the number of particles of WO₃ to that of
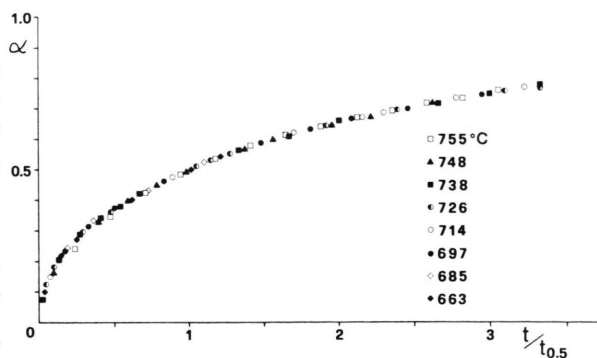

Fig. 1. Fraction reacted, α, plotted vs. reduced time $(t/t_{0.5})$ for 1 : 1 WO₃−SrCO₃ mixture at various reaction temperatures.

SrCO$_3$ amounts to about 830) showed that the only solid reaction product is the normal tungstate in stoichiometric amount.

The experimental α (ratios of the weight loss at time t to that at $t = \infty$) are plotted in Fig. 1 for the different isothermal runs versus the reduced time $t/t_{0.5}$ ($t_{0.5}$ being the t value when $\alpha = 0.5$). All the data can be fitted with a single curve, over the explored range of α.

Since in the present case the mechanism based on cation counterdiffusion was shown to be effective by the experiments carried out according to Wagner's procedure, a suitable means for treating the experimental data was thought to be Dünwald-Wagner's equation [3]:

$$\alpha = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\{-n^2 K t\}$$

where $K = \pi^2 D/R^2$; D = diffusion coefficient; R = radius of the coated spheres.

The above equation was originally proposed for the study of reactions between a solid phase formed with spherical particles of uniform radius and a gaseous phase, whenever the slowest step in the process is diffusion into or out of the solid particles. However, it was also commonly applied to solid-solid reactions and proved particularly useful in certain cases governed by cation counterdiffusion such as spinel formation reactions [9].
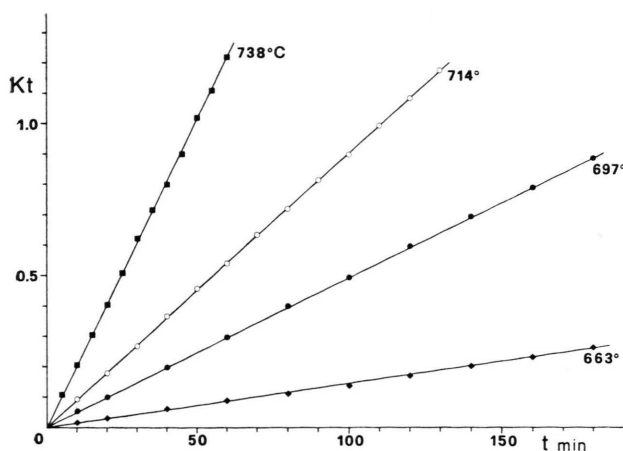

Fig. 2. Plots of $K t$ vs. t for some of the studied isotherms.

* The values of $K t$ as a function of α have been interpolated from those tabulated by Giess [10].

Typical plots of $K t$* versus t for some of the isotherms studied are reported in Fig. 2: the experimental data satisfy Dünwald-Wagner's equation over the entire range studied. The same good fitting was observed with all the other isotherms.

Finally, Fig. 3 shows a straightline dependence of $\log K$ on $1/T$, according to the equation

$$\log K = 13.45 - 69.994/4.576\,T$$
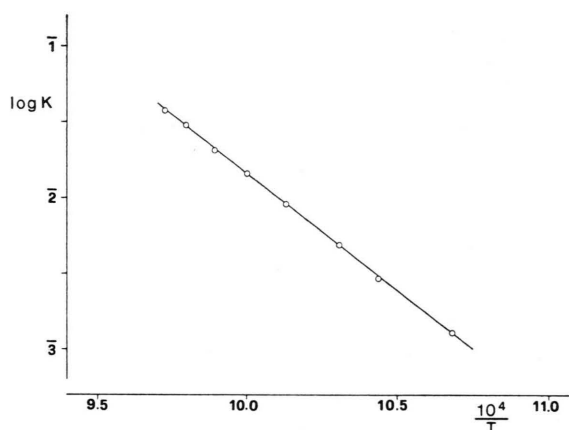
where K is expressed in min^{-1}.

Fig. 3. Arrhenius plot for 1 : 1 WO$_3$–SrCO$_3$ mixture.

Previous results [1] concerning the reaction of MoO$_3$ with SrCO$_3$ showed that the formation of SrMoO$_4$ proceeds at a markedly lower temperature ($412°$ – $498\,°C$) than is found in the present work for SrWO$_4$; further, the formation of SrMoO$_4$ is governed by the diffusion of a single species (Mo^{6+}) [11], not by cation counterdiffusion.

Considering that Mo^{6+} and W^{6+} have the same value of the ionic radius (0.62 Å), and that both SrMoO$_4$ and SrWO$_4$ have the same scheelite type structure with almost identical values of the cell volume (349.6 and 350.0 Å^3) [12], it appears reasonable to emphasise the difference in the Tammann-temperatures of MoO$_3$ (280 °C) and WO$_3$ (635 °C). This might account for the much lower temperature range for SrMoO$_4$ formation. On the other hand, at such lower temperature the Sr^{2+} ion would not possess a sufficient mobility (since the Tammann-temperature for SrCO$_3$ is 647 °C) and therefore would not be allowed to take part as diffusing species in the reaction between MoO$_3$ and SrCO$_3$.

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