Mechanism of $CaMoO_4$ Formation in the Solid State from CaO and MoO_3

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The formation in the solid state of $CaMoO_4$ from CaO (single crystal) and MoO_3 was investigated by the contact method in the temperature range 625–710 °C and at $10^{-4} < p_{O_2} < 1$ atm.

The relatively high velocity of this process compared with that for $CaWO_4$ formation is explained on the basis of the different types of lattice disorder predominant in the two reaction products.

As concerns $CaMoO_4$, the majority defect pair $(V_{Mo}^{6'}, h^{\cdot})$ was deduced by Wagner and Schmalzried's method.

The overall results indicate that the rate-determining step of $CaMoO_4$ formation is the molybdenum diffusion via $V_{Mo}^{6'}$.

In previous papers we have studied the kinetics of $CaWO_4$ formation from CaO (single crystals) and WO_3 (pellets) [1] and from Ca_3WO_6 and WO_3 (both in pellets) [2], the contact method being used.

By means of kinetic measurements carried out under different oxygen partial pressures and with inert marker determinations it was possible to show that the process in both cases procedes by diffusion of W^{6+} and O^{2-} ions [1, 2].

As for the reaction $CaO + WO_3 \rightarrow CaWO_4$, on the basis of the crystal structure, the predominant lattice disorder $(V_0{}^{2\cdot}, O_i{}^{2'})$* proposed by Ridgon and Grace [3] and the diffusion coefficient values, a reaction mechanism was suggested which involves as rate-determining step the diffusion of the oxygen via $V_0{}^{2\cdot}$ [1].

The present work reports the results obtained for $CaMoO_4$ formation in the temperature range 625–710 °C employing the diffusion couples method; CaO single crystal plates ($5 \times 5 \times 0.5$ mm) cut along the (100) plane from an "Atomergic Chemetals Co." specimen and MoO_3 (Alfa Inorganics 99.9%) pellets prefired at 600 °C were used.

Results and Discussion

In Fig. 1 the Arrhenius trend of the kinetic constant k ($cm^2\,sec^{-1}$) as obtained in air for $CaMoO_4$ formation is compared with that given in Ref. [1] for $CaWO_4$ (curves a and b respectively).

In the case of molybdate $\log k$ depends linearly on $1/T$ according to the equation

$$\log k = 1.46 - 54{,}226/4.576\,T\,.$$

Kinetic measurements were also performed at 700 °C in the $10^{-3} \leqq p_{O_2} \leqq 1$ atm range. The k values increase with oxygen partial pressure: $k \propto p_{O_2}^{1/n}$ with $n = 6 \pm 1$.

In order to obtain further information on the $CaMoO_4$ synthesis, inert marker (Pt ribbons 5 µm thick) tests were also carried out in the above mentioned p_{O_2} range. At the end of the reaction time the markers were observed at the interface $CaMoO_4 | MoO_3$, so indicating that the transport mechanism involves the diffusion of molybdenum and oxygen.

A formal comparison between curves a and b of Fig. 1 indicates that the $CaMoO_4$ formation is faster than the $CaWO_4$ one (because of the high vapour pressure of MoO_3 even at 700 °C the two reactions were studied in different temperature ranges). This result is unexpected since both compounds show the same structure (scheelite) with very similar lattice parameters [5]. Moreover the diffusion coefficients (as determined in $CaMoO_4$ and $CaWO_4$

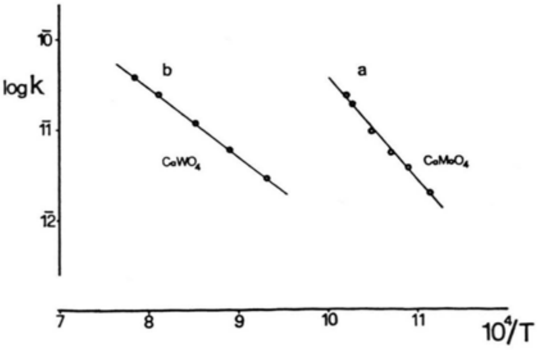

Fig. 1. Arrhenius plots for: a) $CaMoO_4$ formation, b) $CaWO_4$ formation.

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* These point defects are written in the notation used by Kröger-Vink [4].

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single crystals at 800 °C) are close for Ca^{2+} ($7.6 \cdot 10^{-15}$ and $7.0 \cdot 10^{-15}$ cm^2 sec^{-1}, respectively) while those for Mo^{6+} and W^{6+} coincide ($1.0 \cdot 10^{-13}$ cm^2 sec^{-1}) [6].

Some considerations can be made in order to give an explanation of the above results.

The dependence of the kinetic constant on p_{O_2}, as observed in $CaMoO_4$ formation, allows to exclude that oxygen diffusion is the rate-determining step; in fact in an oxygen diffusion via vacancies the reaction rate should decrease with increasing p_{O_2} as observed for $CaWO_4$.

Furthermore, by considering that the activation energy for $CaMoO_4$ synthesis ($E = 54$ kcal mole^{-1}) is practically coincident with that for the molybdenum diffusion in $CaMoO_4$ ($E = 53$ kcal mole^{-1}) [7] it can be supposed that molybdenum diffusion represents the rate-determining step. The apparently high mobility of the oxygen ions which follows from such a mechanism might be explained by transport through the gas phase toward the reaction interface.

A deeper insight into the different kinetic behaviour observed in the two reactions could be gained by individuating the predominant lattice disorder present in $CaMoO_4$. This can be accomplished by extending the method proposed by Wagner and Schmalzried [8] for the spinels to the ABO_4 compounds. For $CaMoO_4$, which is a p-type semiconductor [9, 10], the values of the partial logarithmic derivatives $(\partial \ln [h^\cdot]/\partial \ln p_{O_2})_T$ for all possible majority defect pairs were calculated and then compared with those obtained from electrical conductivity measurements $(\partial \ln \sigma/\partial \ln p_{O_2})_T$. The latter were performed by Zhukovskii and Petrov [9] on single crystal $CaMoO_4$ samples in the oxygen partial pressure range 10^{-4}—1 atm. From their data $(\partial \ln \sigma/\partial \ln p_{O_2})_T = 0.2$.

It can be easily verified that only the majority defect pairs $O_i^{2'}$, $h^\cdot$ and $V_B^{6'}$, $h^\cdot$ give for the derivative $(\partial \ln [h^\cdot]/\partial \ln p_{O_2})_T$ values satisfactorily close to 0.2, as shown hereafter under a) and b) respectively.

a) Let us consider the crystal-gas equilibrium

$$1/2\, O_{2(g)} \rightleftarrows O_i^{2'} + 2\, h^\cdot \qquad (1)$$

with the constant

$$K_1 = [O_i^{2'}]\,[h^\cdot]^2\, p_{O_2}^{-1/2}\,.$$

From the simplified electroneutrality condition

$$2\,[O_i^{2'}] \cong [h^\cdot]$$

it follows

$$[h^\cdot] = 2^{1/3}\, K_1^{1/3}\, p_{O_2}^{1/6}\,, \quad \text{hence} \quad \sigma \propto p_{O_2}^{1/6}\,.$$

b) Let us consider the crystal-gas equilibrium

$$AO_{(s)} + 3/2\, O_{2(g)} + B_B \rightleftarrows V_B^{6'} + 6\, h^\cdot + ABO_{4(s)} \qquad (2)$$

with the constant

$$K_2 = [V_B^{6'}]\,[h^\cdot]^6\, p_{O_2}^{-3/2}\,.$$

From the simplified electroneutrality condition

$$6\,[V_B^{6'}] \cong [h^\cdot]$$

it follows

$$[h^\cdot] = 6^{1/7}\, K_2^{1/7}\, p_{O_2}^{3/14}\,,$$

hence $\sigma \propto p_{O_2}^{3/14}$ and $[V_B^{6'}] \propto p_{O_2}^{3/14}$.

The comparison of the values calculated for the cases a) (0.17) and b) (0.21) with the experimental one, although not allowing a sure choice, seems to indicate that the majority defect pair is $V_B^{6'}$, $h^\cdot$. In order to individuate the reaction mechanism, one can underline that both models leave out as majority defect the oxygen vacancies and that in case b) fully ionized molybdenum vacancies are present. Taking also into account the trend of the kinetic constant as a function of p_{O_2}, it may be concluded that the kinetics of $CaMoO_4$ formation is governed by the diffusion of Mo^{6+} via $V_{Mo}^{6'}$.

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