Mechanism of CaMoO₄ Formation in the Solid State from CaO and MoO₃

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The formation in the solid state of CaMoO₄ from CaO (single crystal) and MoO₃ was investigated by the contact method in the temperature range 625–710 °C and at 10⁻⁴ < p₂O < 1 atm.

The relatively high velocity of this process compared with that for CaW₀₄ formation is explained on the basis of the different types of lattice disorder predominant in the two reaction products.

As concerns CaMoO₄, the majority defect pair (V⁺Mo, h₋) was deduced by Wagner and Schmalzried’s method.

The overall results indicate that the rate-determining step of CaMoO₄ formation is the molybdenum diffusion via V⁺Mo.

In previous papers we have studied the kinetics of CaWO₄ formation from CaO (single crystals) and WO₃ (pellets) [1] and from Ca₃W₀₆ and WO₃ (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 proceeds by diffusion of W⁺ and O₂⁻ ions [1, 2].

As for the reaction CaO + WO₃ → CaWO₄, on the basis of the crystal structure, the predominant lattice disorder (V₀₂⁺, O₂⁻)* 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 V₀₂⁺ [1].

The present work reports the results obtained for CaMoO₄ formation in the temperature range 625–710 °C employing the diffusion couples method;

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

Results and Discussion

In Fig. 1 the Arrhenius trend of the kinetic constant k (cm² sec⁻¹) as obtained in air for CaMoO₄ formation is compared with that given in Ref. [1] for CaWO₄ (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 ≤ p₂O ≤ 1 atm range. The k values increase with oxygen partial pressure: \( k \propto p_{O₂}^{1/n} \) with \( n = 6 \pm 1 \).

In order to obtain further information on the CaMoO₄ synthesis, inert marker (Pt ribbons 5 μm thick) tests were also carried out in the above mentioned p₂O range. At the end of the reaction time the markers were observed at the interface CaMoO₄|MoO₃, 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 CaMoO₄ formation is faster than the CaWO₄ one (because of the high vapour pressure of MoO₃ 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 CaMoO₄ and CaWO₄
single crystals at 800 °C) are close for Ca\(^{2+}\) (7.6 \(\times\) 10\(^{-15}\) and 7.0 \(\times\) 10\(^{-15}\) cm\(^2\) sec\(^{-1}\), respectively) while those for Mo\(^{6+}\) and W\(^{6+}\) coincide (1.0 \(\times\) 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 CaMo\(_4\) 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 CaMo\(_4\) synthesis \((E = 54\) kcal mole\(^{-1}\)) is practically coincident with that for the molybdenum diffusion in CaMo\(_4\) \((E = 53\) 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 CaMo\(_4\). This can be accomplished by extending the method proposed by Wagner and Schmalzried [8] for the spinels to the ABO\(_4\) compounds. For CaMo\(_4\), which is a p-type semiconductor [9, 10], the values of the partial logarithmic derivatives \((\partial \ln \sigma / \partial \ln p_{O_2})_T\) 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 CaMo\(_4\) 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 \(O_1^{2+}\), \(h\) and \(V_{B^6}^\prime\), \(h\) give for the derivative \((\partial \ln [h^\prime] / \partial \ln p_{O_2})_T\) values satisfactorily close to 0.2, as shown hereafter under a) and b) respectively.

a) Let us consider the crystal-gas equilibrium
\[
\frac{1}{2} O_2(g) \leftrightarrow O_2^{2+} + 2 h^\prime
\]  
with the constant
\[
K_1 = [O_2^{2+}] [h^\prime]^2 p_{O_2}^{1/2}.
\]

From the simplified electroneutrality condition
\[
2 [O_2^{2+}] \approx [h^\prime]
\]

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

b) Let us consider the crystal-gas equilibrium
\[
A_0(s) + 3/2 O_2(g) + B^6 \leftrightarrow V_{B^6} + 6 h^\prime + ABO_4(g)
\]

with the constant
\[
K_2 = [V_{B^6}] [h^\prime]^6 p_{O_2}^{-3/2}.
\]

From the simplified electroneutrality condition
\[
6 [V_{B^6}] \approx [h^\prime]
\]

it follows
\[
[h^\prime] = 6^{1/7} K_2^{1/7} p_{O_2}^{3/14},
\]

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 \(V_{B^6}, h^\prime\). In order to individuate the reactions 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 CaMo\(_4\) formation is governed by the diffusion of Mo\(^{6+}\) via \(V_{Mo}\).