On the Mechanism of CaWO₄ Formation in the Solid State from CaO and WO₃

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The formation in the solid state of CaWO₄ from CaO (single crystal) or Ca₃WO₆ and WO₃ was investigated by the contact method between 800 and 1000 °C in air and in argon.

The results obtained indicate that these reactions are governed by the diffusion of the W⁴⁺ and O²⁻ ions.

From the CaWO₄ structure, along with the lattice disorder predominant in this compound (0 vacancies and 0 interstitials) and the values of ionic mobilities, it was possible to state that the oxygen diffusion, via V₆⁺, represents the rate-determining step in the considered reactions.

The spinel formation reactions in the solid state from the corresponding oxides were extensively studied recently it was stated that all these reactions are governed by a cation counter-diffusion mechanism.

On the contrary, the analogous formation reactions of other important compounds, e.g. silicates, titanates, molybdates and particularly tungstates, were scarcely investigated.

In a previous paper, two of us investigated the reaction between MgO and WO₃ in which MgWO₄ is the only product formed: it was possible to state that this process follows a linear rate law in the very early stage and a parabolic law with a cation counter-diffusion mechanism in the subsequent stages.

This work reports the results obtained on the reaction between CaO and WO₃: the main product formed, Ca₃WO₆ (scheelite), differs in its structure from the wolframite structure of MgWO₄ and also in its electrical properties (CaWO₄ is an electronic conductor while MgWO₄ is a predominantly ionic conductor).

Since in the reaction between CaO and WO₃ the compound Ca₃WO₆ can also be formed, as proved by the corresponding phase diagram, some measurements were carried out also on the reaction Ca₃WO₆ + 2 WO₃ → 3 CaWO₄.

The kinetic process was investigated employing the diffusion couples method in the temperature range 800–1000 °C under air and argon: CaO single crystal plates (5·5·0.5 mm) cut along the (100) plane from an “Atomergic Chemetals Co.” specimen, WO₃ (Koch-Light 99.9%) and Ca₃WO₆ pellets (8 mm wide and ~1.5 mm thick) were used.

The Ca₃WO₆ was prepared according to Belyaev et al.

Apparatus and techniques were already described in previous works.

Results

The reaction between CaO single crystals and WO₃ pellets has been studied in air at several temperatures between 800 and 1000 °C.

Microscopic observation on sections obtained by cutting the couples parallel to the diffusion direction showed that the formed product was made up by two layers of different textures; the first one, adherent to WO₃, was white and much thicker than the second one, which looked like a transparent solid in contact with CaO. Owing to the smallness of this layer the evaluation of the layer thickness ratio was rather difficult.

In the determinations at higher temperatures, owing to the relatively large volatility of WO₃, the reaction products were formed also on the CaO surfaces not in contact with solid WO₃; the layers observed had a larger (although not reproducible) thickness than the one formed at the interface CaO(xe) / WO₃(pellet).

X-ray diffraction analysis of the product surfaces in contact with the WO₃ pellets showed the CaWO₄ reflections only: the relative intensities were in good agreement with those reported in the corresponding ASTM “identification card”.

Repetition of the analysis of the product surfaces which adhered to the CaO crystals showed also the reflections of Ca₃WO₆. In particular the intensities corresponding to the (002), (004), (006) planes were much higher than those of the Ca₃WO₆ observed had a larger (although not reproducible) thickness than the one formed at the interface CaO(xe) / WO₃(pellet).
reported in the ASTM "identification card" of Ca₃W₀₆, while those corresponding to the (200) and (020) planes were depressed.

A comparison between the two patterns (Fig. 1) allowed to deduce that the product had grown on the CaO surface (f. c. c.; a = 4.810 Å) preferably oriented along the (001) direction. Such results may be explained considering that the Ca₃W₀₆ cell is monoclinic with the following lattice parameters: a = 5.547 Å; b = 5.808 Å; c = 8.002 Å; β = 90.15°.

In some cases the interfaces between CaO (sc) and WO₃ (pellet) were marked with Pt ribbons (≈ 100 microns wide and ≈ 5 microns thick); at the end of the reaction time the product layer was included between the CaO crystal and the Pt markers: these were in contact with the WO₃ pellet (Figure 2 a).

![Fig. 1. X-ray diffraction patterns of Ca₃WO₆: a) from our sample; b) from the ASTM "identification card".](image)

![Fig. 2. Schemes for the CaWO₄ formation mechanism.](image)

From the total thickness values of the product layer (x) vs. time (t) (Fig. 3) for the five studied isotherms, the kinetic constants, k, reported in Table 1 were deduced, using the parabolic law in the form \( x^2 = 2k t \).

![Fig. 3. Isotherms for the reaction between CaO (sc) and WO₃ (pellet) in air.](image)

![Fig. 4. Isotherms at 960 °C for the reaction between CaO (sc) and WO₃ (pellet).](image)

The \( \log k \) values show a linear dependence on \( 1/T \) according to the equation

\[
\log k = -5.31 - 29.954/4.576 T.
\]

Some kinetic determinations have been carried out under argon. As an example, the isotherm obtained at 960 °C is reported in Fig. 4 and compared with the corresponding isotherm obtained under air: the decrease of the O₂ partial pressure increases the process rate. The \( k_{\text{argon}} \) value was \( 3.4 \times 10^{-11} \text{cm}^2 \text{sec}^{-1} \).

Finally, the reacting system Ca₃WO₆ | WO₃ was investigated under air at 800 °C: the kinetic constant obtained was \( k = 1.5 \times 10^{-12} \text{cm}^2 \text{sec}^{-1} \). In some cases the reaction interfaces were marked: at the end of the reaction time the Pt ribbons were at the interface CaWO₄ | WO₃ (Figure 2 b).
Discussion
From the results obtained by the marker experiments it is apparent that the transport mechanism governing the CaWO$_4$ formation involves the diffusion of the tungsten ion and of oxygen; moreover the comparison between the two isotherms at 960 °C in air and in argon indicates that the oxygen is transported at the CaO/CaWO$_4$ interface as an ion and not as O$_2$ via the gas phase.

This mechanism, different from that observed for the MgWO$_4$ formation reaction, may be discussed in terms of the CaWO$_4$ structure and of the lattice disorder predominant in this compound, along with the transport and thermodynamic properties.

In the CaWO$_4$ structure (scheelite) which may be regarded as a cubic close-packed array of Ca$^{2+}$ and WO$_4^{2-}$ units$^6$, the oxygen ions are not close-packed: therefore, from a structural point of view it becomes possible for the oxygen ions to diffuse through the CaWO$_4$ compound.

Rigdon and Grace$^7$ deduced that the main lattice disorder in CaWO$_4$ involves O vacancies (V$_O^-$), O interstitials (O$_I^{2+}$) and conduction electrons: the latter are present only as minority defects though carrying the bulk of the current ($0.92 < \xi < 0.99$ at 1000 °C).

On the basis of the defect model proposed by these authors, the oxygen vacancies in CaWO$_4$ are involved in the following equilibria:

\[
\begin{align*}
\text{nil} & \rightleftharpoons V_{Ca}^o + V_{W}^o + 4 V_{O}^o \\
O_{o} & \rightleftharpoons O_{I}^{2+} + V_{O}^o \\
O_{o} & \rightleftharpoons V_{O}^o + 2 e^+ + 1/2 O_2 .
\end{align*}
\]

From the last equation it is seen that as the oxygen pressure decreases the amount of oxygen vacancies $V_{O}^o$ increases. The isotherm at 960 °C shows that the reaction rate under argon is larger than under air, thus supporting the assumption of a reaction mechanism which involves, as rate-determining step, the diffusion of the oxygen via $V_{O}^o$.

By means of Wagner and Schmalzried's theory$^1$ it is possible to obtain the average value of the diffusion coefficient for the rate-determining species, in this case $D_{O^+}$, by the equation

\[ D_{O^+} = kR T/\gamma z_{O^+} |\Delta G^0| \]  

(1)

where

\[ k = \text{rate constant in cm}^2\text{sec}^{-1} ; \]
\[ \gamma = \text{numerical factor the value of which depends on the reaction mechanism} ; \]
\[ \Delta G^0 = \text{molar standard free energy of the considered reaction} . \]

In the present case, Eq. (1) can be applied only to the reaction $\text{Ca}_3\text{WO}_6 + 2\text{WO}_3 \rightarrow 3\text{CaWO}_4$ since in the other reaction between CaO and WO$_3$ two distinct phases are formed (see Fig. 2) so that the constant $k$ for CaWO$_4$ formation in the latter reaction depends also on the kinetic and thermodynamic parameters of the other phase formed$^1^2$.

With the $k$ value determined for the reaction $\text{Ca}_3\text{WO}_6 + 2\text{WO}_3 \rightarrow 3\text{CaWO}_4$ at 800 °C ($1.5 \times 10^{-12}$ cm$^2$ sec$^{-1}$), $\Delta G^0_{1073} = -21,500$ cal/mole$^7$, and $\gamma = 1.5$, Eq. 1) gives $D_{O^+} = 5 \times 10^{-14}$ cm$^2$ sec$^{-1}$. The comparison of this value with those determined at 800 °C$^8$ for the ions W$^{6+}$ ($D = 7 \times 10^{-13}$ cm$^2$ sec$^{-1}$) and Ca$^{2+}$ ($D = 1 \times 10^{-15}$ cm$^2$ sec$^{-1}$) gives for the diffusion coefficients the sequence $D_{W^{6+}} > D_{O^+} > D_{Ca^{2+}}$, which is consistent with the proposed mechanism.