

On the Mechanism of CaWO_4 Formation in the Solid State from CaO and WO_3

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The formation in the solid state of CaWO_4 from CaO (single crystal) or Ca_3WO_6 and WO_3 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 W^{6+} and O^{2-} ions.

From the CaWO_4 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 V_O^{2-} , represents the rate-determining step in the considered reactions.

The spinel formation reactions in the solid state from the corresponding oxides were extensively studied¹; recently it was stated that all these reactions are governed by a cation counter-diffusion mechanism².

On the contrary, the analogous formation reactions of other important compounds, e.g. silicates, titanates, molybdates and particularly tungstates, were scarcely investigated^{3–5}.

In a previous paper⁵, two of us investigated the reaction between MgO and WO_3 in which MgWO_4 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 WO_3 : the main product formed, CaWO_4 (scheelite), differs in its structure from the wolframite structure of MgWO_4 ⁶ and also in its electrical properties (CaWO_4 is an electronic conductor⁷ while MgWO_4 is a predominantly ionic conductor⁵).

Since in the reaction between CaO and WO_3 the compound Ca_3WO_6 can also be formed, as proved from the corresponding phase diagram⁸, some measurements were carried out also on the reaction $\text{Ca}_3\text{WO}_6 + 2 \text{WO}_3 \rightarrow 3 \text{CaWO}_4$.

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, WO_3 (Koch-Light 99.9%) and Ca_3WO_6 pellets (8 mm wide and ~1.5 mm thick) were used.

The Ca_3WO_6 was prepared according to Belyaev et al.⁹

Apparatus and techniques were already described in previous works¹⁰.

Results

The reaction between CaO single crystals and WO_3 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 WO_3 , 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 WO_3 , the reaction products were formed also on the CaO surfaces not in contact with solid WO_3 ; the layers observed had a larger (although not reproducible) thickness than the one formed at the interface $\text{CaO}_{(\text{sc})} | \text{WO}_{3(\text{pellet})}$.

X-ray diffraction analysis of the product surfaces in contact with the WO_3 pellets showed the CaWO_4 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 Ca_3WO_6 . In particular the intensities corresponding to the (002), (004), (006) planes were much higher than those

reported in the ASTM "identification card" of Ca_3WO_6 , 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

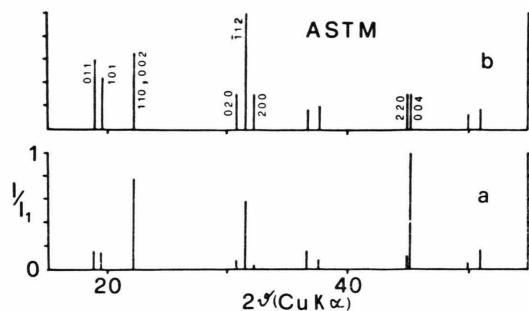


Fig. 1. X-ray diffraction patterns of Ca_3WO_6 : a) from our sample; b) from the ASTM "identification card".

CaO surface (f. c. c.; $a = 4.810 \text{ \AA}$) preferably oriented along the $\langle 001 \rangle$ direction. Such results may be explained considering that the Ca_3WO_6 cell is monoclinic with the following lattice parameters: $a = 5.547 \text{ \AA}$; $b = 5.808 \text{ \AA}$; $c = 8.002 \text{ \AA}$; $\beta = 90.15^\circ$.

In some cases the interfaces between $\text{CaO}_{(\text{sc})}$ and $\text{WO}_3(\text{pellet})$ 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 WO_3 pellet (Figure 2 a).

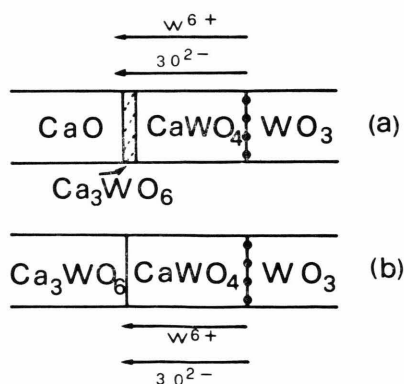


Fig. 2. Schemes for the CaWO_4 formation mechanism.

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 $x^2 = 2kt$.

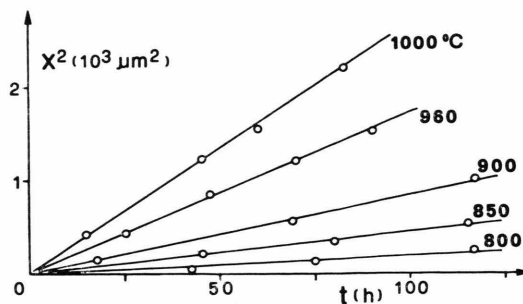


Fig. 3. Isotherms for the reaction between $\text{CaO}_{(\text{sc})}$ and $\text{WO}_3(\text{pellet})$ in air.

T/K	$k/\text{cm}^2 \text{sec}^{-1}$
1073	$2.9 \cdot 10^{-12}$
1123	$6.1 \cdot 10^{-12}$
1173	$1.2 \cdot 10^{-11}$
1233	$2.5 \cdot 10^{-11}$
1273	$3.8 \cdot 10^{-11}$

Table 1

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

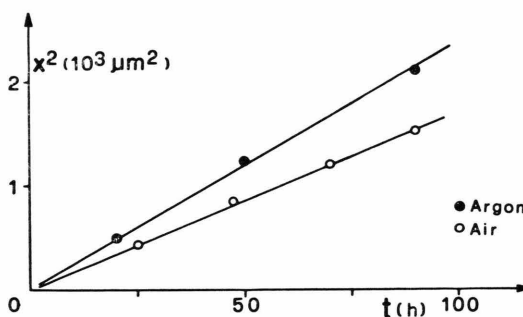


Fig. 4. Isotherms at 960°C for the reaction between $\text{CaO}_{(\text{sc})}$ and $\text{WO}_3(\text{pellet})$.

with the corresponding isotherm obtained under air: the decrease of the O_2 partial pressure increases the process rate. The k_{argon} value was $3.4 \cdot 10^{-11} \text{ cm}^2 \text{sec}^{-1}$.

Finally, the reacting system $\text{Ca}_3\text{WO}_6|\text{WO}_3$ was investigated under air at 800°C : the kinetic constant obtained was $k = 1.5 \cdot 10^{-12} \text{ cm}^2 \text{sec}^{-1}$. In some cases the reaction interfaces were marked: at the end of the reaction time the Pt ribbons were at the interface $\text{CaWO}_4|\text{WO}_3$ (Figure 2 b).

Discussion

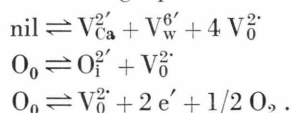
From the results obtained by the marker experiments it is apparent that the transport mechanism governing the CaWO₄ formation involves the diffusion of the tungsten ion and of oxygen; moreover the comparison between the two isotherms at 960 °C in air and in argon indicates that the oxygen is transported at the CaO|CaWO₄ interface as an ion and not as O₂ via the gas phase.

This mechanism, different from that observed for the MgWO₄ formation reaction, may be discussed in terms of the CaWO₄ structure and of the lattice disorder predominant in this compound, along with the transport and thermodynamic properties.

In the CaWO₄ structure (scheelite) which may be regarded as a cubic close-packed array of Ca²⁺ and WO₄²⁻ units⁶, 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 CaWO₄ compound.

Rigdon and Grace⁷ deduced that the main lattice disorder in CaWO₄ involves O vacancies (V_O²⁻), O interstitials (O_i²⁺) and conduction electrons: the latter are present only as minority defects though carrying the bulk of the current (0.92 < t_e < 0.99 at 1000 °C).

On the basis of the defect model proposed by these authors, the oxygen vacancies in CaWO₄ are involved in the following equilibria:



From the last equation it is seen that as the oxygen pressure decreases the amount of oxygen

vacancies V_O²⁻ 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_O²⁻.

By means of Wagner and Schmalzried's theory¹¹ it is possible to obtain the average value of the diffusion coefficient for the rate-determining species, in this case D_{O²⁻}, by the equation

$$D_{\text{O}^{2-}} = k RT / \gamma z_{\text{O}^{2-}} | \Delta G^0 | \quad (1)$$

where

- k = rate constant in cm² sec⁻¹;
- γ = numerical factor the value of which depends on the reaction mechanism;
- ΔG^0 = molar standard free energy of the considered reaction.

In the present case, Eq. (1) can be applied only to the reaction Ca₃WO₆ + 2 WO₃ → 3 CaWO₄ since in the other reaction between CaO and WO₃ two distinct phases are formed (see Fig. 2) so that the constant k for CaWO₄ formation in the latter reaction depends also on the kinetic and thermodynamic parameters of the other phase formed¹².

With the k value determined for the reaction CaWO₆ + 2 WO₃ → 3 CaWO₄ at 800 °C (1.5 · 10⁻¹² cm² sec⁻¹), $\Delta G_{1073}^0 = -21,500$ cal/mole¹³, and $\gamma = 1.5$, Eq. (1) gives $D_{\text{O}^{2-}} = 5 \cdot 10^{-14}$ cm² sec⁻¹. The comparison of this value with those determined at 800 °C¹⁴ for the ions W⁶⁺ ($D = 7 \cdot 10^{-13}$ cm² sec⁻¹) and Ca²⁺ ($D = 1 \cdot 10^{-15}$ cm² sec⁻¹) gives for the diffusion coefficients the sequence $D_{\text{W}^{6+}} > D_{\text{O}^{2-}} > D_{\text{Ca}^{2+}}$, which is consistent with the proposed mechanism.

¹ H. Schmalzried, Solid State Reactions, Academic Press Inc., 1974, p. 90.

² W. Laqua and B. Reuter, J. Solid State Chem. **9**, 24 [1974].

³ K. Pschera and K. Hauffe, Z. anorg. All. Chem. **264**, 217 [1951].

⁴ V. Leute, Z. physik. Chem. N. F. **48**, 319 [1951].

⁵ G. Flor and R. Riccardi, Z. Naturforsch. **31 a**, 619 [1976].

⁶ A. W. Sleight, Acta Cryst. **B 28**, 2899 [1972].

⁷ M. A. Rigdon and R. E. Grace, J. Amer. Chem. Soc. **56**, 475 [1973].

⁸ L. L. Y. Chang, M. G. Scroger, and B. Phillips, J. Amer. Ceram. Soc. **49**, 387 [1966].

⁹ I. N. Belyaev, V. S. Filip'ev, and E. G. Fesenko, Zh. Strukt. Khim. **4**, 719 [1963].

¹⁰ G. Flor, V. Massarotti, and R. Riccardi, Z. Naturforsch. **29 a**, 503 [1974]; G. Flor, V. Massarotti, and R. Riccardi, Z. Naturforsch. **30 a**, 304 [1975].

¹¹ C. Wagner, Z. phys. Chem. **B 34**, 309 [1936]; H. Schmalzried, Z. physik. Chem. N. F. **33**, 111 [1962].

¹² A. D. Pelton, H. Schmalzried, and C. D. Greskovich, Ber. Bunsenges. physik. Chem. **76**, 543 [1972].

¹³ T. N. Rezhukhina, V. A. Levitskii, and M. Ya. Frenkel, Izv. Akad. Nauk SSSR, Neorg. Mater. **2**, 325 [1966].

¹⁴ V. M. Zhukovskii, V. N. Popova, and A. S. Zhukovskaya, Izv. Akad. Nauk SSSR, Neorg. Mater. **9**, 992 [1973].