# Kinetics of $MgWO_4$ Formation in the Solid State Reaction between MgO and $WO_3$

Giorgio Flor and Riccardo Riccardi

Centro di studio per la termodinamica ed elettrochimica dei sistemi salini fusi e solidi del CNR.
Institute of Physical Chemistry, University of Pavia (Italy)

(Z. Naturforsch. **31 a**, 619—621 [1976]; received April 2, 1976)

The solid state reaction of $MgWO_4$ formation from MgO (single crystals) and $WO_3$ was investigated in the temperature range 800—985 °C under both air and argon atmosphere.

The techniques employed for the kinetic study (contact and thermogravimetric methods) allowed to point out that the process follows the linear rate law in the early stages and the parabolic one in the subsequent stages.

From inert marker experiments, kinetic determinations under the two different atmospheres and conductivity measurements, it was possible to state that the reaction is governed by a cation counter-diffusion mechanism.

In the last years the tungstates of bivalent metals have found a growing interest owing to their many technical applications. Since these tungstates are generally prepared from the oxides[1], a systematic study of the kinetics and mechanism of the corresponding reactions in the solid state might be useful.

The present paper deals with the reaction between MoO and $WO_3$ in which $MgWO_4$ is the only product formed, as proved from the relevant phase diagram[2].

The kinetic process was investigated by the contact method in the $800-985$ °C temperature range, using single crystals of MgO and sintered pellets of $WO_3$. In order to determine the reaction mechanism the inert marker method was used. To obtain information on the type of conduction involved in $MgWO_4$, dc and ac conductivity measurements were performed.

## Experimental

*MgO*. Single crystal plates ($5 \times 5 \times 0.5$ mm) were obtained by cleavage along the (100) planes from a MgO (Atomergic Chemetals Co.) specimen.

*$WO_3$*. Pellets (8 mm wide and $\sim 1.5$ mm thick) were prepared by pressing the powder (Koch-Light 99.9%) at $10^3$ kg/cm$^2$ and then sintering it for 5 h at 900 °C.

*$MgWO_4$*. A stoichiometric powder mixture of MgO (C. Erba RS) and $WO_3$ was fired for 30 h at 850 °C (in a sealed quartz vessel) and 50 h at 1000 °C (in a platinum crucible), with repeated mixing during the heating period. X-ray analysis of the obtained product showed the typical reflections of $MgWO_4$ only.

Using pellets obtained by pressing the above product between two platinum powder layers, electrical conductivity measurements were performed in the temperature range $800-960$ °C. The ac conductivity (total conductivity) was measured with a Wayne-Kerr autobalance bridge B 331, the dc conductivity (an estimate of the electronic contribution) was determined in a way similar to that employed by Rigdon and Grace on $CaWO_4$[3]. From the ratio between the dc and ac values it was possible to estimate the electronic transference numbers ($t_e$), the values of which ranged between 0.1 and 0.2 and increased with the temperature.

The kinetic measurements (contact method) were carried out under air and argon with the apparatus and techniques described in previous works[4].

Moreover, in order to observe the early stage of the formation reaction, a few thermogravimetric determinations were performed with a Du Pont "950 Thermogravimetric Analyzer" at 900 °C, a temperature at which $WO_3$ already shows a significant volatility[5]. Single crystals of MgO suspended at the balance arm by means of a very thin Pt wire, were surrounded by a quartz crucible with the inner walls coated with $WO_3$; the $MgWO_4$ formation from solid MgO and $WO_3$ vapour was detected by recording the mass increase of the suspended crystals as a function of time.

## Results and Discussion

The results obtained by the contact method in the temperature range $800-985$ °C are reported in Fig. 1 as $x^2$ ($x =$ average thickness of the product

Reprint requests to Prof. Riccardo Riccardi, Istituto di Chimica Fisica, Università di Pavia, *I-27100 Pavia* (Italy).

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

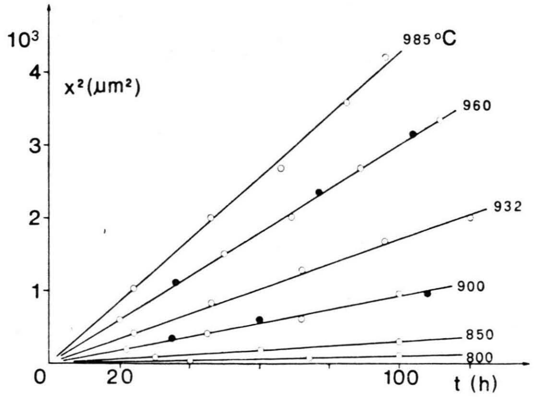

Fig. 1. Isotherms for the reaction $MgO_{(sc)} + WO_{3(pellet)} \rightarrow MgWO_4$. Open circles: air atmosphere; filled circles: argon atmosphere.

layer) vs. $t$ (time); the course of the reaction clearly is not influenced by the absence of $O_2$ in the atmosphere surrounding the reaction couples at least in the considered temperature range.

Since the plots show a fairly good linear trend, the practical reaction rate constant $k$ of the parabolic law, $x^2 = 2\,k\,t$, can be evaluated. The $\log k$ values in turn show a linear dependence on $1/T$ according to the equation

$$\log k = -0.99 - \frac{53{,}061}{4.576\,T}$$

where $k$ is expressed in cm²/sec and $T$ in K.

For what concerns the thermogravimetric measurements at 900 °C, in Fig. 2 are reported as a function of $t$ (for the early minutes), both the mass increase of MgO per unit surface area ($\Delta m/S$) and a quantity which can be easily calculated from the latter, i. e., the thickness ($x$) of the $MgWO_4$ formed: the plot shows that within the first 5 minutes the process is governed by a linear law.

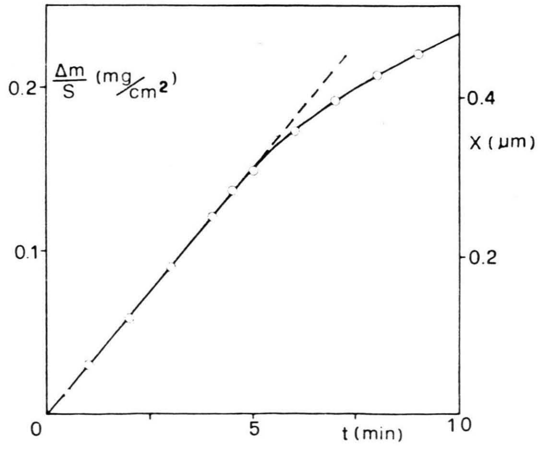

Fig. 2. TG measurement at 900 °C for the reaction $MgO_{(sc)} + WO_{3(vap)} \rightarrow MgWO_4$ (early stages).

The experimental data allowed to detect a clear parabolic rate law only for $t > 20$ min. The $k$ value ($4.0 \cdot 10^{-12}$ cm²/sec), which can be evaluated starting from this time on, is smaller than that obtained at the same temperature by the contact method ($1.3 \cdot 10^{-11}$ cm²/sec); the difference might be accounted for by the fact that the vapour pressure of $WO_3$ at 900 °C is relatively low (activity $a_{WO_3} < 1$ at the MgO surface).

In order to obtain information on the reaction mechanism, diffusion couples $MgO_{(sc)} | WO_{3(pellet)}$, with Pt wire markers, were heated for 120 h at 960 °C. Microscopic observation on sections obtained by cutting the couples parallel to the diffusion direction, showed that the marker position divided the product (60 μm thick) into two layers of different textures (Fig. 3), the first of which, in contact with MgO, being white and the second, in contact with $WO_3$, light brown. The total thickness of the product layer was too small to allow an accurate estimate of the ratio between the two layers: however the brown layer was, on the average, three times thicker than the white one.

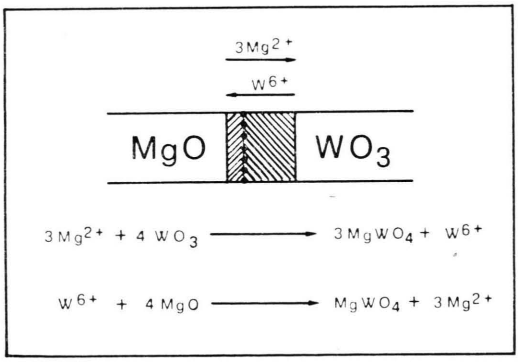

Fig. 3. Scheme for $MgWO_4$ formation mechanism.

Owing to the relatively large $WO_3$ volatility, the reaction product was formed also on the MgO surfaces not in contact with solid $WO_3$: the corresponding layer (white) was slightly less thick (55 μm) than that formed at the interface $MgO_{(sc)} | WO_{3(pellet)}$.

X-ray diffraction analysis on the product surface which was in contact with the MgO single crystal brought into evidence only a few reflections of remarkable intensity corresponding to the (010), (020) and (100), (200) planes of $MgWO_4$ (wolframite type structure with cell parameters: $a = 4.687$ Å; $b = 5.675$ Å; $c = 4.928$ Å; $\beta = 90.71°$ [6]). A comparison between the relative intensities observed and those reported on the ASTM "Identification Card" of $MgWO_4$, allowed to deduce that this product had grown on the MgO surface (f.c.c.; $a = 4.273$ Å) preferably oriented along the $\langle 010 \rangle$-direction.

On the contrary, X-ray analysis on the product surface which adhered to the $WO_3$ pellet showed a random orientation.

On the basis of the present results it is possible to deduce the following conclusions.

In the early stage (five minutes at 900 °C) the rate of $MgWO_4$ formation is predominantly determined by the phase-boundary reaction [7] and successively by the diffusion through the product layer.

The mechanism governing the reaction between $MgO_{(s\,c)}$ and $WO_{3(\text{pellet})}$ is the cation counter-diffusion according to the reaction scheme shown in Figure 3.

This conclusion, directly drawn by means of the marker experiments at 960 °C, is in agreement with the results obtained in the kinetic determinations, under air and argon (Fig. 1), from which a mechanism requiring an oxygen transport via gas phase can be excluded. Moreover, since in the wolframite structure of $MgWO_4$ the oxygens are hexagonally close-paked [6], it can be deduced that oxygen does not behave as a diffusing species in the reaction product.

Also the conductivity measurements from which it was possible to classify $MgWO_4$ as a predominantly ionic conductor (at least in the 800 – 960 °C temperature range) are formally in agreement with the proposed mechanism.

---

[1] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Green and Co. 1931, Vol. XI, p. 782 ff.

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

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

[4] G. Flor, V. Massarotti, and R. Riccardi, Z. Naturforsch. **29 a**, 503 [1974].

[5] V. Leute, Z. physik. Chem. Neue Folge **48**, 319 [1966].

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

[7] H. Schmalzried, "Solid State Reactions", Academic Press Inc. 1974, p. 99.