Kinetics of the Solid State Reaction between CuO and WO_3

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Z. Naturforsch. **35a**, 332–335 (1980); received November 24, 1979

The solid state reaction of $CuWO_{4-x}$ formation from CuO and WO_3 was studied by the contact method in air and nitrogen. The results showed that the reaction is governed by the diffusion of the W^{6+} and O^{2-} ions and that the rate determining step is the diffusion of oxygen ions in the reaction product. This is in agreement with the defect structure of copper tungstate, an *n*-type semiconductor with oxygen vacancies through which the diffusion process is possible.

The formation of the tungstates of magnesium and calcium by solid state reaction between WO_3 and the corresponding oxide was recently investigated by Flor et al. [1, 2] using the contact method. A divalent metal tungstate, the copper one, has been successfully employed as cathode material in primary batteries based on lithium anode and organic electrolyte [3]. It appeared therefore of interest to us to study the kinetics of formation of this compound in the temperature range (670 – 710 °C) in which it is obtained in practice and where the contact method can be applied.

The only kinetic investigation on this system has been performed by Leute [4], who studied the reaction between powdered CuO and a WO_3 single crystal.

Experimental

CuO and WO_3 reagent grade were used as received, after drying.

The pellets to be used in the measurements were obtained by pressing the powders in a die having a diameter of 1.20 cm at a pressure of 350 MPa.

Pellets of the reactants were put into contact in a boron nitride holder; the pressure on the pellets was adjusted and kept constant by means of a calibrated spring external to the furnace. The silica container was of the type commonly used in our laboratory for high temperature conductivity measurements [5]. A furnace (Heraeus ROK/A-4/30) was employed, the temperature of which was controlled by means of a Kelvitron TPG programmer.

At the end of each experiment the samples were sectioned by microtome and observed at a metallographic microscope (Reichert MeF 2).

X-ray diffraction analyses (powder method) were performed by a JEOL Mod. JDX-85 diffractometer, using the CuK α radiation.

Results

In all the experiments the reaction product showed poor adherence to WO_3, so that two separate

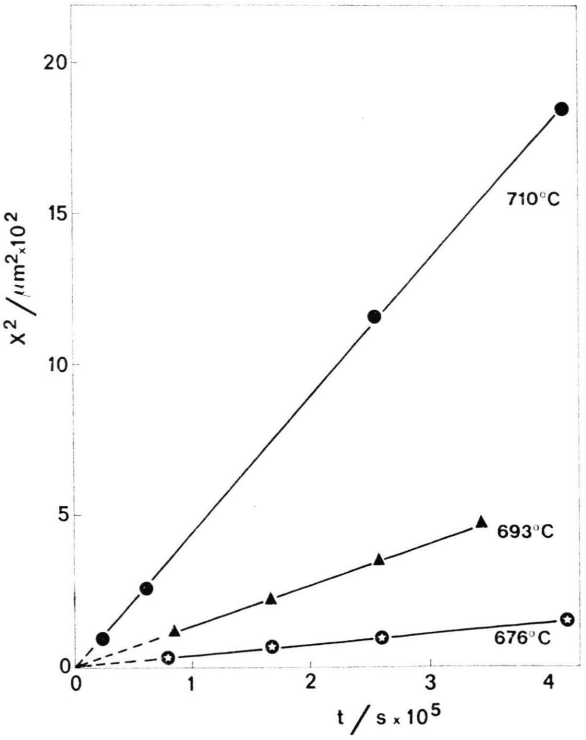

Fig. 1. Isotherms (square of the layer thickness as a function of time) for the solid state reaction, in air, $CuO + WO_3 \rightarrow CuWO_4$.

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Table 1. Kinetic constants for the three isotherms studied.

t °C	$10^3/T$ K^{-1}	k $cm^2 \times s^{-1}$
676	1.054	3.675×10^{-12}
693	1.035	1.351×10^{-11}
710	1.017	4.500×10^{-11}

pellets were obtained: the WO_3 one, the surface of which was perfectly clean, and the CuO one, the surface of which originally in contact with WO_3 was covered with a layer of reaction product. The thickness of the latter was generally uniform over the whole pellet and could be easily measured, due to its marked difference in colour (orange) with respect to CuO (black).

The reaction product showed X-ray diffraction patterns identical to those of the non-stoichiometric compound $CuWO_{4-x}$ studied by Gebert and Kihlborg [6]. In some experiments, platinum ribbons about 5 µm thick were inserted at the interphase between the two reactants; at the end of the experiment the marker was always found at the interphase between the reaction product and WO_3.

The experiments were performed in air and in nitrogen. In Fig. 1 the values of the square of the average thickness X of the reaction product have been plotted vs. t for the temperatures of 676 °C, 693 °C, and 710 °C, in air. The experimental points fall onto straight lines and therefore Tammann's parabolic law [7] is obeyed. By putting the latter in the usual form $X^2 = 2\,k\,t$, values of the kinetic constant k (Table 1) are obtained. These show an Arrhenius-type dependence on the reciprocal temperature (Fig. 2), according to the equation

$$\log k = 19.56 - \frac{134{,}571}{4.576\,T},$$

where k is in $cm^2\ s^{-1}$ and T in K.

The influence of the environment, air or nitrogen, on the reaction kinetics is shown in Fig. 3, where the isotherms obtained at 710 °C are reported: the increase in oxygen partial pressure decreases the reaction rate.

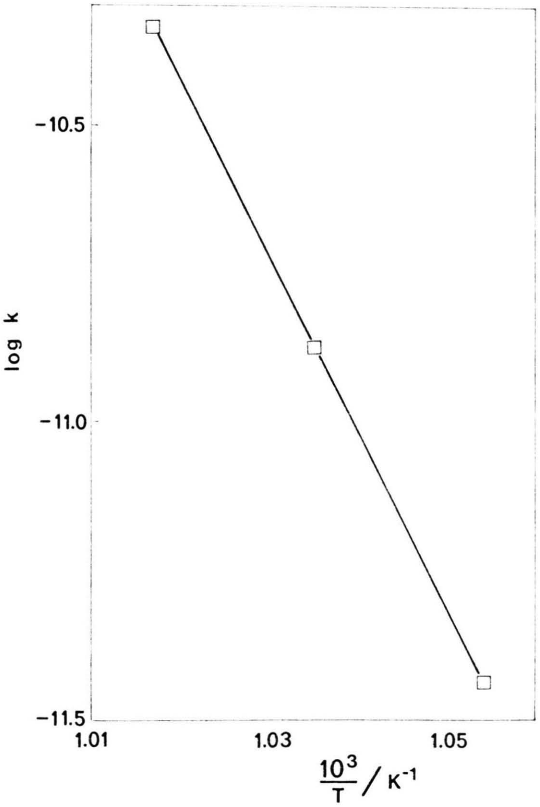

Fig. 2. Arrhenius plot for the kinetic constant for the solid state reaction, in air, $CuO + WO_3 \rightarrow CuWO_4$ (k in $cm^2\ s^{-1}$).

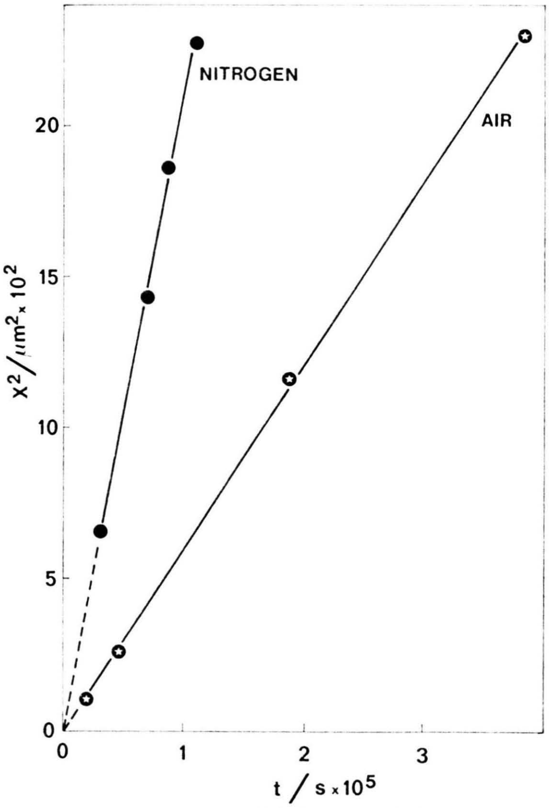

Fig. 3. Isotherms at 710 °C for the solid state reaction, in air and nitrogen, $CuO + WO_3 \rightarrow CuWO_4$.

Discussion

The formation mechanism of $CuWO_{4-x}$ by solid state reaction of CuO and WO_3 is governed by the diffusion of W^{6+} and oxygen, as shown by the marker experiments. The observed influence of the oxygen partial pressure on the reaction rate indicates that oxygen reaches the interphase $CuO/CuWO_4$ as an ion and not as $O_2(g)$. The mechanism is schematically shown in Figure 4.

In agreement with the sizes of the diffusing species (the relevant ionic radii are $r_{O^{2-}} = 1.40\,Å > r_{W^{6+}} = 0.62\,Å$) the rate determining step should be the diffusion of oxygen ions. However, to discuss in more detail the diffusion process in the reaction product, it is necessary to have some insight into the structure of the copper tungstate. $CuWO_{4-x}$ is triclinic and is characterized by a distorted wolframite-type structure [6], which differs from that of wolframite in that all the angles in the unit cell differ from 90°. The wolframite-type structure is monoclinic; it has been observed for several tungstates, such as those of magnesium, manganese, iron, cobalt, nickel, zinc and cadmium. According to Gebert and Kihlborg [6], in the structure of $CuWO_{4-x}$ both the copper and the tungsten ions are coordinated to six oxygen ions in a distorted octohedron. Furthermore, the ratio Cu/W is close to unity, while oxygen is deficient with respect to the formula $CuWO_4$. The dependence of the conductivity on oxygen partial pressure [8] indicates that the compound is an *n*-type semiconductor having O^- and O^{2-} vacancies in its lattice: the former should be involved in the low temperature range, the latter in the high temperature range. The temperature range explored was 0 – 600 °C.

These observations lead to the conclusion that oxygen vacancies as well as conduction electrons are present in the $CuWO_{4-x}$ lattice and that diffusion of oxygen ions in the compound is possible. The defect situation in the temperature range here considered can be represented by the equation

$$O_0 \rightleftarrows V_0^{2\cdot} + 2\,e' + \tfrac{1}{2}\,O_2\,.$$

Therefore a decrease in oxygen partial pressure causes an increase of the number of oxygen vacancies and thus of the reaction rate. This is in agreement with the experimental results and with the assumption that the diffusion of oxygen ions by the vacancy mechanism is the rate determining step.

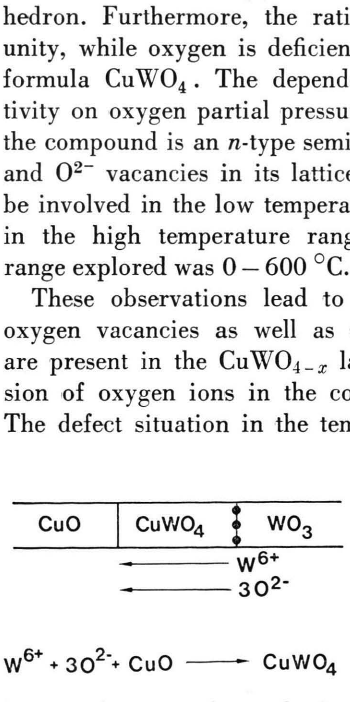

Fig. 4. Scheme for the mechanism of $CuWO_4$ formation.

Comparison of the present conclusions with those reached by Flor et al. for the solid state formation of $MgWO_4$ [1] and $CaWO_4$ [2] emphasizes the importance of the structure as well as of the defect situation of the reaction products in deciding the reaction mechanism. In fact in $MgWO_4$ diffusion of the oxygen ions, closely packed in the wolframite-type structure [9], is extremely unlikely and cation counterdiffusion [1] ought to be the actual mechanism. $CaWO_4$, on the other hand, has a scheelite structure with a cubic array of densely packed Ca^{2+} and WO_4^{2-}, while the oxygen ions are loosely packed [9]. According to Rigdon and Grace [10], most defects are either oxygen ion vacancies or interstitials. The structure therefore allows the diffusion of the oxygen ions in the reaction product. The kinetic results support these conclusions and, similarly to what we observed (although for different reasons) for the $CuWO_{4-x}$ formation, the diffusion in the compound of both the tungsten and oxygen ions is possible, the latter process being the rate determining one [2].

In the present case, the average value of the diffusion coefficient of the rate determining species, i. e. of the oxygen ion, can be calculated by the following equation deduced by Wagner [11] and Schmalzried [12]:

$$D_{O^{2-}} = \frac{k\,R\,T}{\gamma\, z_{O^{2-}}\,|\Delta G^0|}$$

where k is the rate constant; R the gas constant; T the absolute temperature; z the valency of the diffusing species; ΔG^0 the Gibbs free energy in standard conditions for the formation of one mole of $CuWO_{4-x}$ from CuO and WO_3; γ a numerical factor the value of which depends on the reaction mechanism: in the present case $\gamma\, z_{O^{2-}} = 8/9$. The ΔG^0 value for the formation of $CuWO_{4-x}$ is not known but since the Gibbs free energy and the enthalpy values for the formation from the elements in standard conditions at 25 °C of CuO, WO_3 [13, 14] and

$CuWO_4$ [15] were available, approximate values of ΔG^0 for the relevant reaction could be calculated at different temperatures, with the assumption that ΔH^0 is constant. Thus $D_{O^{2-}}$ values of 0.6, 3.0 and 7.0×10^{-12} cm^2 s^{-1} at the temperatures of 676 °C, 693 °C and 710 °C, respectively, were deduced from the above equation. A value lower by about two orders of magnitude (0.5×10^{-13} cm^2 s^{-1} at 800 °C) has been obtained by Flor et al. [2] for $D_{O^{2-}}$ in $CaWO_4$. The difference might be justified by the different defect structures of the two materials.

The results obtained lead to the conclusion that $D_{W^{6+}} > D_{O^{2-}} > D_{Cu^{2+}}$ and consequently that the rate determining step is not the chemical one (which would be important during the early stage of the reaction, not considered here) but the oxygen ion diffusion in the reaction product.

Leute, who employed in his experiments a WO_3 single crystal, ascertained that (after an induction time) the thickness of the product layer increased according to a parabolic law in the temperature range 690 – 805 °C. Although the nature of the diffusing species has not been determined, this author's results could be interpreted by the mechanism proposed in the present paper.

Acknowledgements

Fruitful discussions with G. Flor, V. Massarotti and R. Riccardi are gratefully acknowledged.

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