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The interface transport of V_2O_5 and WO_3 into $CaMo(W)O_4$ stimulated by an electric field

A. Guseva, A. Neiman^{*}, E. Konisheva, M. Trifonova, E. Gorbunova

Chemical Department, Ural State University, Ekaterinburg 620083, Russia

Abstract

An electric field applied to the CaWO₄/V₂O₅, CaMoO₄/V₂O₅ and CaMoO₄/WO₃ systems causes grain boundary and surface transports of oxides having a low surface energy (V₂O₅ and WO₃) and their segregation on the grain surface. It was found that V₂O₅ penetrates to the inner surface of CaWO₄ much more intensively when the V₂O₅ briquette bears a negative potential: $(-)V_2O_5|CaWO_4(+)$. The penetration of V₂O₅ and WO₃ to the inner surface of the CaMoO₄ ceramic is accompanied by a chemical interaction. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The researchers [1–3] revealed and studied the propagation of solid WO₃ along grain boundaries in CaWO₄ in the absence of a chemical interaction. The moving force of this process is the difference in the surface energies of the contacting solid materials and/or an external electric field. WO₃ has a low surface energy $\alpha_{WO_3} = 1 \times 10^{-5}$ J/cm² [4]. Consequently, the formation of a WO₃ coat on the surface of calcium tungstate grains is favorable in thermodynamic terms. This unusual effect of an "electric surface transport" was detected and analyzed in detail only for the CaWO₄/WO₃ system. However, the study of such interface processes has a great practical significance for producing supported catalytic and composite materials [5].

In our study the diffusants were WO₃ and, in addition, V₂O₅, which also has a low surface energy $\alpha_{V_2O_5} = 0.9 \times 10^{-5}$ J/cm² [4]. The CaMoO₄ and CaWO₄ ceramics (the former is isostructural to the latter) served as the substrates. Thus, CaWO₄/V₂O₅, CaMoO₄/V₂O₅ and CaMoO₄/WO₃ systems were analyzed.

2. Experimental

The effect of an electric field on the rate of the solid-phase grain boundary impregnation was studied by the method of contact annealing of ceramic briquettes with an external potential difference applied to the reaction cell [2]. The processes were monitored by observing the change in the mass of the contacting briquettes and measuring the thickness of the colored layer of the formed composite in an MBS-9 optical microscope (magnification up to $56 \times$). The morphology of the ceramics was analyzed in a JSM-3 electron

^{*} Corresponding author: Tel.: +007-3432-617-470; fax: +007-3432-615-978.

E-mail address: arkady.neiman@usu.ru (A. Neiman).

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microscope (magnification up to $10\,000\times$). The chemical composition of the grain boundary impregnation products was determined using the X-ray diffraction analysis (DRON-2 diffractometer, Co-k_a radiation), X-ray microprobe (Superprobe-JCXA-733) and Raman spectroscopic (MOLE microprobe) techniques. The composition of the surface of the ceramic grains was analyzed by the ESCA method (HP 5950 A spectrometer). A Rigaku–Denki microthermal analyzer was used for the differential thermal analyzer. The heating rate was 5 °C/min. The calcium concentration of the tungsten oxide briquette was measured by the complexonometric titration.

3. Results and discussion

The experiments were performed at 600 $^{\circ}$ C in the following cells:

$$(-)\mathbf{Pt}|\mathbf{V}_{2}\mathbf{O}_{5}|\mathbf{CaWO}_{4}|\mathbf{V}_{2}\mathbf{O}_{5}|\mathbf{Pt}(+), \tag{1}$$

$$\begin{array}{l} (-) Pt |V_2 O_5| Ca MoO_4 |Pt(+) \ U > 0, \\ (+) Pt |V_2 O_5| Ca MoO_4 |Pt(-) \ U < 0 \end{array} \tag{2}$$

and at 900 °C in the following cell:

$$(-)Pt|WO_3|CaMoO_4|Pt(+) U > 0,$$

(+)Pt|WO_3|CaMoO_4|Pt(-) U < 0 (3)

A voltage of 300 V was applied to the cells (1) and (2) and up to 150 V to the cell (3). The current density did not exceed 1 mA in the cells (1) and (2) and 4 mA in (3).

CaMoO₄ and CaWO₄ are mixed (O^{2-} ,e)-conductors [6,7] and V₂O₅ (WO₃) are semiconductors [8]. Therefore at an electric current passed through the cells (1)–(3) the only electrochemical process is reaction of oxygen oxidation or reduction

$$(+)\mathbf{O}^{2-} \rightarrow \frac{1}{2}\mathbf{O}_{2-} + 2\mathbf{e}$$

$$(-)^{\frac{1}{2}} O_2 + 2e \rightarrow O^{2-}$$

at the interfaces $V_2O_5|CaMo(W)O_4$, $WO_3|CaWO_4$ and $CaMo(W)O_4|Pt$.

After experiments these regions were thoroughly investigated and it was found that chemical composition of products was the same either for spontaneous or current conditions. It means that no additional, current induced, internal reaction was occurred.

Processes in the cells (1)–(3) are substantially different, therefore we shall consider theirs separately.

3.1. Spreading of V_2O_5 along grain boundaries in the CaWO₄ ceramic

After the experiments, the V_2O_5 and $CaWO_4$ briquettes were separated and weighed. In all the cases the mass of the cathodic $V_2O_5^{(-)}$ briquette decreased, while the mass of the $CaWO_4$ briquette increased correspondingly. The mass of the anodic part $V_2O_5^{(+)}$ changed little. The mass of the $CaWO_4$ increased linearly with the quantity of the electricity passed through the cell (1), Fig. 1.

The cathodic region of the white CaWO₄ briquette turned brown-orange in color. The ESCA method showed that the [V]/[W] ratio on the surface of the CaWO₄ grains was 0.57. The X-ray microprobe analysis also revealed the presence of vanadium in the calcium tungstate briquette (Fig. 2). The vanadium concentration was especially large on the CaWO₄ surface on the cathode side and decreased towards the anode. The X-ray diffraction analysis of the CaWO₄ briquette did not



Fig. 1. CaWO₄ briquette mass increase vs. the quantity of the electricity passed through the cell (1). T = 600 °C, U = 300 V.



Fig. 2. X-ray microprobe analysis of a CaWO₄ sample annealed in contact with V₂O₅ in the cell (1). Q = 280 C, t = 600 °C, $\tau = 54$ h. The cross-section of the sample was made at a distance of 100 µm from the surface coming in contact with V₂O₅⁽⁻⁾.

reveal any other phases except CaWO₄. This was due to the fact that the maximum concentration of the vanadium oxide in the CaWO₄ briquette did not exceed 1.6 mass% (even when a charge of 280 °C was passed through the cell).

The phase diagram of the $CaWO_4-V_2O_5$ system has been unclear. Therefore we analyzed the reaction

$$CaWO_4 + V_2O_5 \rightarrow CaV_2O_6 + WO_3 \tag{4}$$

thermodynamics. This reaction was chosen as the most probable on the following grounds. In accordance with [9], at the temperature adopted in our experiments (600 °C) CaV₂O₆ was formed as the only product in the CaO/V₂O₅ mixture. Ca₃-(VO₄)₃ and Ca₂V₂O₇ appeared at a higher temperature. The calculation yielded $\Delta G_{(3)}^0 = +31$ kJ/mole. This result suggests a small probability of a chemical interaction in the cell (1).



Fig. 3. DTA curve for equimolar mixture CaWO₄ and V₂O₅.

To check the probability that a liquid phase was formed in the CaWO₄/V₂O₅ system at 600 °C, a DTA curve was measured for an equimolar mixture of CaWO₄ and V₂O₅ (Fig. 3). No thermal effects were detected at 600 °C. The endoeffect at 660 °C was due to the melting of individual V₂O₅. The preceding stage showed however that some V₂O₅ spread on the surface of the CaWO₄ substrate was in an amorphitized glassy-like state at the experimental temperature (600 °C). This state is well known and is characteristic of mixed phases containing a large quantity of vanadium, molybdenum or tungsten oxide [10].

So, our experimental data suggest that the solid-phase vanadium oxide spreads over the grain boundaries in the calcium tungstate ceramic in the cell (1) as is the case in the CaWO₄/WO₃ system [2,3]. The process can be visualized as the transport of some negatively charged form of V_2O_5 . Two possible mechanisms of the electric surface transport (electroosmotic migration and solid-phase electrocapillarity) were considered in Ref. [2].

Considering the size (13 μ m) of the CaWO₄ grains (determined by the electron microscopy), the mass and depth of V₂O₅ penetrating into the CaWO₄ ceramic briquette (thickness of the colored layer), the average thickness of the V₂O₅ film on the surface of CaWO₄ grains was estimated at

 \approx 7 nm for the composite containing 0.16 mass% V₂O₅. This thickness corresponds to ~10 monolayers of V₂O₅.

3.2. Spreading of V_2O_5 along grain boundaries in the CaMoO₄ ceramic

In the cell (2), as in (1), V_2O_5 penetrated into the bulk of the CaMoO₄ briquette. However, this process was accompanied by a solid-phase interaction of CaMoO₄ and V_2O_5 by the equation:

$$xCaMoO_4 + V_2O_5 \rightarrow xCaO + V_2O_5 \cdot xMoO_3.$$
 (5)

This conclusion was supported by the fact that the annealed CaMoO₄ briquette was colored orange due to the penetration of V₂O₅. The X-ray diffraction analysis revealed the presence of CaO on the surface of the CaMoO₄ briquette coming in contact with the V₂O₅ briquette. A dark-gray layer appeared on the surface of the V₂O₅ briquette contacting CaMoO₄. In accordance with the X-ray diffraction analysis, this layer was a solid solution of the molybdenum oxide in the vanadium oxide (Fig. 4).

Although the phase composition changed, the mass of the annealed V_2O_5 and $CaMoO_4$ briquettes remained constant at any direction of the current and, also, in the absence of an external voltage. From the last observation it follows that a counter-diffusion of the MoO₃ and V_2O_5 components took place in the cell (2).



Fig. 4. The scheme of products layers formation in the cell (2).

So, the penetration of the diffusant into the $CaMoO_4$ ceramic in the cell (2) was accompanied by a chemical interaction of the starting materials.

3.3. Spreading of WO_3 along grain boundaries in the $CaMoO_4$ ceramic

In the cell (3), as in (1) and (2), WO₃ penetrated into the bulk of the CaMoO₄ ceramic. At a temperature above 700 °C the following reaction occurred:

$$CaMoO_{4 sol} + WO_{3 sol} = CaWO_{4 sol} + MoO_{3 gas}.$$
(6)

It is known that MoO_3 melts at 795 °C [11] and is sublimated intensively at 650 °C [12]. Therefore all MoO_3 , which was formed by the reaction (6), volatilized at the experimental temperature (900 °C).

The mass of the CaMoO₄ briquettes increased and the mass of the WO₃ briquettes decreased in all the experiments. When the polarization direction was reversed from -U to +U, the increase in the mass of the CaMoO₄ briquettes was greater (Fig. 5). The phase compositions differed a little at -U and +U.

When U > 0, the X-ray diffraction analysis revealed the presence of WO₃ on the CaMoO₄ briquette. From the Raman spectroscopic data it followed that CaWO₄ was formed simultaneously (Table 1). The intensity of the main lines of CaWO₄ in the Raman spectrum of the sample diminished smoothly with the distance from the interface to the



Fig. 5. Change in the mass of the CaMoO₄ briquettes vs. the applied voltage in the cell (3). T = 900 °C, $\tau = 6$ h.

Ord. no.	Sample	X-ray diffraction analysis	Raman spectroscopy
1	$CaMoO_4 (U = 0 V, 900 °C, 36 h)$	CaMoO ₄ , WO ₃	CaMoO ₄ , CaWO ₄ ,
	with CaMoO ₄ , 500 µm removed	CaMoO ₄	CaMoO ₄ , CaWO ₄
2	CaMoO ₄ ($U = +95$ V, 900 °C, 59 h, $Q = 28$ C)	CaMoO ₄ , WO ₃	CaMoO ₄ , CaWO ₄
	with $CaMoO_4$, 350 µm removed	CaMoO ₄	CaMoO ₄ , CaWO ₄
3	CaMoO ₄ ($U = -95$ V, 900 °C, 20 h, $Q = 113$ C)	CaMoO ₄ , WO ₃	CaMoO ₄
	with CaMoO ₄ , 400 µm removed	CaMoO ₄	CaMoO ₄

Table 1 Results of the layer-by-layer X-ray diffraction analysis and Raman spectroscopy at t = 25 °C

bulk of the CaMoO₄ ceramic. The WO₃ briquette turned dark-green in color and grew darker with the experimental time. The complexometric titration revealed the presence of calcium in the WO₃ briquette. So, when U > 0, two processes took place: a segregation of WO₃ on the grain boundaries in CaMoO₄ and a chemical interaction resulting in the formation of CaWO₄.

When U < 0, a loose white layer up to 1.1 mm thick appeared on the CaMoO₄ briquette coming in contact with WO₃ ($\tau = 6$ h, -150 V). The nearcontact region of this white layer contained WO₃ and CaMoO₄ (Table 1). In accordance with the Raman spectroscopic data, CaWO₄ was not formed at U < 0. One may suppose the formation of a distributed system, in which CaMoO₄ grains were covered with a thin film of the highly conducting WO₃ phase. This supposition is confirmed indirectly by the following considerations. If WO₃ spreads over the grain surface (thanks to a lower surface energy [4]), the initial ceramic may become more brittle. This was actually the case at U < 0. The WO₃ briquette turned light-green in color. Calcium was not detected in the WO₃ briquette.

So, when U < 0, the main process was the spreading of the tungsten oxide on the surface of the CaMoO₄ ceramic grains.

The mean diameter of the CaMoO₄ ceramic grains was 13 μ m. By use of above-mentioned technique we have estimated the average thickness of the WO₃ film as \approx 8 nm. This value corresponds to \sim 20 mono-layers of WO₃.

4. Conclusion

It was found that an oxide $(V_2O_5 \text{ or } WO_3)$ having a low surface energy segregates on grain

boundaries of a complex ceramic in the CaWO₄/ V_2O_5 , CaMoO₄/ V_2O_5 and CaMoO₄/ WO_3 systems studied. Hence, the field-stimulated transport of the oxide with a low surface energy to the inner surface of another oxide is rather general.

The solid-phase transport of V_2O_5 in the CaWO₄/V₂O₅ system is not complicated by a chemical interaction. The transport rate increases sharply for $(-)V_2O_5|CaWO_4(+)$ thanks to the electroosmotic transport or electrocapillarity. The propagation of V₂O₅ and WO₃ on the internal surface of the CaMoO₄ ceramic in the CaMoO₄/V₂O₅ and CaMoO₄/WO₃ systems is accompanied by a chemical interaction at inner interfaces.

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