Wolfram Tantalum and Wolfram Niobium Oxides of the M_nO_{3n-2}(ReO₃) Series

PÁL GADÓ,* BO HOLMBERG and
ARNE MAGNÉLI

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The wolfram oxide $WO_{2.95}$ has recently been shown to possess a structure with periodic crystallographic shear present in a ReO₃-type arrangement of atoms. The character of the shear plane is the same as the one previously observed in $W_{20}O_{58}$. The formula $W_{40}O_{118}$ of the new oxide was derived from the stoichiometric composition determined by chemical analysis, the observed density, and crystallographic data including X-ray single-crystal and powder photographs.[1]

X-Ray investigations of heterogeneous, non-equilibrium samples obtained by heating wolfram trioxide with minor additions of tantala or niobia suggested the existence of ternary phases closely related to $W_{40}O_{118}$. Attempts to prepare these mixed oxides in a pure state in quantities necessary for chemical analysis and for density measurements were unsuccessful. A single crystal obtained from a preparation with a nominal content of 2 mole % of tantala was, however, found to give Weissenberg photographs very similar to those of $W_{40}O_{118}$.

Two of the parameters of the monoclinic unit cell of the wolfram tantalum oxide were easily found, *viz.* $a = 12.0$ and $b = 3.830$ Å. The corresponding values are $a = 11.9$, $b = 3.815$ Å for $W_{40}O_{118}$ and $a = 12.05$, $b = 3.767$ Å for $W_{20}O_{58}$.[2] As the a and b axes define the plane of shear the close agreement between these quantities shows that the shear mechanism present in the mixed oxide is the same as in the two binary wolfram oxides. The extent of edge-sharing between metal-oxygen octahedra characteristic of this

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* On leave of absence from the Industrial Research Institute for Electronics "HIKI", Department of Material Testing, Budapest, Hungary.

particular kind of shear requires that the formula of the material satisfies the general expression M_nO_{3n-2} ($n =$ integer).[2]

The value of n in the above expression corresponds to the number of metal-oxygen octahedra determining the spacing of the shear planes. As estimated from the Weissenberg photographs this should be nearly the same in the mixed oxide as in $W_{40}O_{118}$. The peculiar appearance of the X-ray patterns given by this kind of structures with reflections of observable intensities only within the immediate surroundings of the reciprocal lattice points of the basic ReO₃-type sub-cell, makes the separate determination of the c and β parameters difficult. This is particularly so in the present case where no analysis or density data are available to supplement the crystallographic information. The value of $c \sin \beta$ is, however, obtainable with a fair accuracy. This quantity although not having such strict crystallographic significance as c, gives a direct measure of the distance between the shear planes. The following values were obtained:

	$c \sin \beta$	$(c \sin \beta)/n$
$W_{20}O_{58}$	23.5 Å	1.175 Å
W-Ta-oxide	46.0 Å	
$W_{40}O_{118}$	47.4 Å	1.185 Å

The quotient between $c \sin \beta$ and n, which represents the average contribution per metal atom to the spacing of the shear planes, is nearly the same for the two wolfram oxides. (Analogous observations have been made for the various members of the molybdenum and molybdenum wolfram oxides of the series M_nO_{3n-1} (ReO₃).[3])

If in the formula M_nO_{3n-2} of the ternary wolfram tantalum oxide n is given the values 38, 39, and 40 the quotient $(c \sin \beta)/n$ will be 1.211, 1.179, and 1.150 Å, respectively. As there seems to be little reason to assume tantalum to behave very differently from wolfram in a structure of this kind these data suggest that the ternary oxide most likely has the formula (W, Ta)₃₉O₁₁₅.

The cell parameters of the structure of (W,Ta)₃₉O₁₁₅ obtained from the Weissenberg photographs are in fair agreement with the "ideal" values required by general expressions previously given.[2] (The space diagonal of the metal-oxygen octahedra is assumed to be 3.750 Å.)

	obs.		ideal.	
a	12.0	Å	11.86	Å
b	3.83	Å	3.750	Å
c	51.4	Å	50.95	Å
β	63.5°		64.07°	

Owing to lack of the necessary analytical information the proportion of wolfram and tantalum in the oxide is not directly accessible. The material, however, does not show any sign of the bluish or black colouring usually accompanying a slight reduction of these metals. It thus seems very probable that both metals are present in their maximum states of valency and that in consequence the formula of the oxide specimen represented by the single crystal studied is $W_{35}Ta_4O_{115}$.

Adjacent members of a structural series such as $M_nO_{3n-2}(ReO_3)$ can, as illustrated above, be distinguished with a fair degree of confidence by their single-crystal photographs even with rather high values of n. In consideration of the very subtle difference in chemical composition, e.g. $MO_{2.9487}$ for $M_{39}O_{115}$ and $MO_{2.9500}$ for $M_{40}O_{118}$ this method seems to be a rather good one. On the other hand the linear, very complicated array of reflexions represented by a powder photograph makes it much more difficult to identify such phases. From a comparison of the powder patterns of $W_{40}O_{118}$ and the heterogeneous samples of wolfram tantalum and wolfram niobium oxides it may be stated that the latter also contains a member of the $M_nO_{3n-2}(ReO_3)$ series. Here the value of n should also be about 40. It is, however, not possible to find the exact figure on the basis of powder data only.

In the case of $WO_{2.95}$ the structural study was performed using several single crystals obtained from a well defined, pure specimen. The structural study described above was based on just one individual crystal from a heterogeneous non-equilibrium sample. The appearance of the powder pattern does not provide a means sensitive enough to decide whether the individual crystal is a true representative of the $M_nO_{3n-2}(ReO_3)$-type material present in the preparation.

The mechanism of formation of complicated shear-type phases as those studied here is not well understood. Experience obtained from studies of the molybdenum and molybdenum wolfram oxides of the series $M_nO_{3n-1}(ReO_3)$ has demonstrated the influence of temperature and of the proportions of the reacting compounds in the formation of such phases.[3,4] Trace amounts of extraneous material may also be of importance as evidenced by a stabilizing effect on the formation of $W_{40}O_{118}$ observed in the presence of minute quantities of potassium, aluminium or nickel.[5]

The present investigation has demonstrated the importance of crystallographic shear, of the type previously found to be present in $W_{20}O_{58}$ and $W_{40}O_{118}$, also in the formation of mixed phases of wolfram trioxide with tantala or niobia. Such phases are thus members of the $M_nO_{3n-2}(ReO_3)$ family. It is rather likely that experimental conditions may have an influence on which particular members of the series are formed.

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