On the Existence of Ternary Transition Metal Oxides

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Among the transition metals Mo, W, Ti—Cu binary oxides with a metallic character are formed by Ti, V, Cr, Mo, W. The TiO and VO phases of the NaCl structure have broad homogeneity ranges, viz. $\text{TiO}_{0.60-1.25}^1$ and $\text{VO}_{0.80-1.20}^2$. The atomic arrangement of the tetragonal $\text{VO}_{0.15-0.25}^3$ phase is closely related to that of the cubic body-centered vanadium metal. The oxides Cr_2O_3 , Mo_3O and W_3O are not isomorphous. The Cr_3O_2 and W_3O_4 phases are of the "ordered" and "disordered" Al5 type respectively. Mo_3O_2 has a BiF_3 structure where only three quarters of the 4 Bi and the 12 F positions of the unit cell of that structure are occupied. The MnO, FeO, CoO, and NiO phases of the B1 type cannot, for several reasons, be characterized as metallic oxides.

The ternary $\text{Me}'\text{—Me}''\text{—O}$ systems where $\text{Me}' = \text{Ti, V, Cr, Mn, Fe, Co, Ni, Cu}$ and $\text{Me}'' = \text{Mo and W}$ have been examined in the present study.

EXPERIMENTAL

All the starting materials used in the present investigation were of fairly high purity, about 99.5 %. The oxides were prepared in two different ways.

A. Finely powdered metals were mixed in different ratios, pressed into small brickettes and sintered in zirconia crucibles in a high frequency vacuum induction furnace at a temperature of about 1 600° C. The alloys were then powdered and carefully oxidized by means of steam in the presence of hydrogen in excess at various temperatures between 600° C and 800° C.

B. Mixtures of a metal oxide $\text{Me}''\text{O}_3$ ($\text{Me}'' = \text{Mo, W}$) and the metals Me' ($\text{Me}' = \text{Ti—Fe}$) and Me'' , or metal oxide $\text{Me}'\text{O}$ ($\text{Me}' = \text{Mn—Ni}$) and Me', Me'' were heated in evacuated and sealed silica tubes at various temperatures between 800° C and 1 100° C for up to two weeks. For $\text{Me}' = \text{Cu}$ the Cu_2O oxide was used. Some of the samples were heated in zirconia crucibles in a vacuum induction furnace at about 1 500° C.

The phase analysis was performed by means of powder photographs taken in focussing cameras of the Guinier type, using monochromatized $\text{CuK}\alpha$ and $\text{CrK}\alpha$ radiation.

SURVEY OF THE RESULTS

The Ti—Mo—O and Ti—W—O systems

No ternary metallic oxides were found to exist in these two systems. Because of the great stability of the binary Ti oxides these were formed during the oxidation process. After all the Ti present in the TiMe'' alloys had been

converted into TiO_2 , Me'' oxides were also formed. The lattice constant of the TiO phase was found to vary between $a = 4.16 \text{ \AA}$ and $a = 4.23 \text{ \AA}$ in the presence of both Mo and W. The solubility of Me'' in TiO could not be determined but is most likely very small.

The V—Mo—O and V—W—O systems

No ternary metallic oxides could be prepared. The oxidation process was of the same nature as for $\text{Me}'' = \text{Ti}$. The lattice constants of the V_4O and VO phases were found to vary between the same limits as obtained in the investigation of the $\text{V—V}_2\text{O}_3$ system².

The Cr—Mo—O and Cr—W—O systems

No true ternary metallic oxides were found to exist. But non-metallic oxides of the composition $(\text{Cr}, \text{Me}'')_2\text{O}_3$ were obtained with the Cr/Me'' ratio probably somewhat greater than unity. The structure of these compounds is related to that of Cr_2O_3 ^{5,6} of the D51 type. For Cr_2O_3 the rhombohedral lattice constants are $a = 5.38 \text{ \AA}$, $\alpha = 56.80^\circ$ and $Z = 2$. If hexagonal crystal axes are chosen for the Cr_2O_3 and $(\text{Cr}, \text{Me}'')_2\text{O}_3$ phases the following relation is valid: $c \sim c_{\text{Cr}_2\text{O}_3}/2$ and $a \sim a_{\text{Cr}_2\text{O}_3}$. The lattice constants of $(\text{Cr}, \text{Me}'')_2\text{O}_3$ are:

Hexagonal axes:

$$\begin{cases} (\text{Cr}, \text{Mo})_2\text{O}_3 & a = 4.937 \text{ \AA}, c = 6.763 \text{ \AA}, c/a = 1.370, V = 142.7 \text{ \AA}^3, Z = 3 \\ (\text{Cr}, \text{W})_2\text{O}_3 & a = 4.938 \text{ \AA}, c = 6.787 \text{ \AA}, c/a = 1.374, V = 143.3 \text{ \AA}^3, Z = 3 \end{cases}$$

Rhombohedral axes:

$$\begin{cases} (\text{Cr}, \text{Mo})_2\text{O}_3 & a = 3.643 \text{ \AA}, \alpha = 85.59^\circ, V = 47.58 \text{ \AA}^3, Z = 1 \\ (\text{Cr}, \text{W})_2\text{O}_3 & a = 3.640 \text{ \AA}, \alpha = 85.43^\circ, V = 47.76 \text{ \AA}^3, Z = 1 \end{cases}$$

According to a preliminary investigation the space-group is D_3^7-R32 with the atoms located in the positions: 2 Me distributed at random in 2 (c) x, x, x ; $\bar{x}, \bar{x}, \bar{x}$ with $x \sim 0.17$ and 3 O in 3 (d) $0, x, \bar{x}$; $\bar{x}, 0, x$; $x, \bar{x}, 0$ with $x \sim 0.47$. It was not possible to determine the values of the x parameters with any accuracy because of the unknown deviation of the Cr/Me'' ratio from unity. The oxygen atoms in Cr_2O_3 and $(\text{Cr}, \text{Me}'')_2\text{O}_3$ are arranged in a deformed hexagonal and strongly deformed cubical close-packing respectively.

No similar oxides were found to exist in the cases of $\text{Me}' = \text{Cr}$ and $\text{Me}'' = \text{Ti}$ or V.

The Mn—Mo—O and Mn—W—O systems

In these two systems ternary oxides with the ideal formula $\text{Mn}_3\text{Me}'_3\text{O}$ were obtained, although the easy formation of MnO prevented their preparation in a pure state. Oxides isomorphous with the high speed steel carbide (η carbide) $\text{Fe}_3\text{W}_3\text{C}$ ^{7,8} have earlier been reported by this author, viz. in the case of $\text{Me}_3'\text{Ti}_3\text{O}$ ⁹ Where $\text{Me}' = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ or Cu .*

The values of the axial lengths measured for the η oxides were $a = 11.07$ — $11.11 \text{ \AA}$ for $\text{Mn}_3\text{Mo}_3\text{O}$ and $a = 11.10$ — $11.13 \text{ \AA}$ for $\text{Mn}_3\text{W}_3\text{O}$, indicating

* η nitrides $\text{Me}_3'\text{Me}_3''\text{N}$, where $\text{Me}' = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and $\text{Me}'' = \text{Mo}$ or W , have also been prepared by the present author. A detailed report will shortly appear elsewhere.

comparatively small homogeneity ranges. For the isomorphous carbides $\text{Mn}_3\text{Mo}_3\text{C}$ and $\text{Mn}_3\text{W}_3\text{C}$ Kuo¹⁰ reports $a = 11.13 \text{ \AA}$ in both cases. When the different radius values of C and O, $0.77 \text{ \AA}$ and $0.60 \text{ \AA}$ respectively, are considered, it seems remarkable that the lattice constants of the η oxides and the η carbides are almost the same.

The $\text{Me}'\text{—Me}''\text{—O}$ systems with $\text{Me}' = \text{Fe}$ or Co and $\text{Me}'' = \text{Mo}$ or W

In these four systems two types of ternary metallic oxides occur, viz. of the η carbide structure and the L'3 type (two metal atoms distributed at random in a hexagonal close-packed unit cell). The latter oxides with the ideal formula $\text{Me}'\text{Me}''\text{O}$ have been described earlier². The following lattice constants were obtained for the η oxides: $\text{Fe}_3\text{Mo}_3\text{O}$ $a = 10.92\text{—}10.95 \text{ \AA}$, $\text{Fe}_3\text{W}_3\text{O}$ $a = 10.95\text{—}10.97 \text{ \AA}$, $\text{Co}_3\text{Mo}_3\text{O}$ $a = 10.86\text{—}10.88 \text{ \AA}$, $\text{Co}_3\text{W}_3\text{O}$ $a = 10.87\text{—}10.90 \text{ \AA}$. The existence of the analogous carbides $\text{Fe}_3\text{Mo}_3\text{C}$ ¹¹, $\text{Fe}_3\text{W}_3\text{C}$ ^{7,8}, $\text{Co}_3\text{Mo}_3\text{C}$ ¹², $\text{Co}_3\text{W}_3\text{C}$ ¹¹ is well established, and the observed lengths of the cube edges are about 1 % greater than for the corresponding η oxides.

No metallic oxides other than those mentioned above could be prepared, but a hexagonal oxide $(\text{Fe}, \text{W})\text{O}_2$ with a structure closely related to that of the monoclinic WO_2 was obtained. The Fe/W ratio could not be determined but appears to lie between $\frac{1}{2}$ and $\frac{1}{3}$. The unit cell dimensions of WO_2 ¹³ are: $a = 5.560 \text{ \AA}$, $b = 4.884 \text{ \AA}$, $c = 5.546 \text{ \AA}$, $\beta = 118.93^\circ$, $V = 131.8 \text{ \AA}^3$, $Z = 4$ and of $(\text{Fe}, \text{W})\text{O}_2$: $a = 11.46 \text{ \AA}$, $c = 4.749 \text{ \AA}$, $c/a = 0.415$, $V = 450.0 \text{ \AA}^3$. The unit cell of $(\text{Fe}, \text{W})\text{O}_2$ is derived from the cell of WO_2 if the symmetry is raised to hexagonal ($\beta = 120^\circ$ so that the monoclinic b axis turns into the hexagonal c axis) and the monoclinic a and c axes are doubled (each turning into a hexagonal a axis). For this reason the probable cell content of $(\text{Fe}, \text{W})\text{O}_2$ is 16 formula units. No systematic absence of reflections were found in the powder photograph.

The Ni—Mo—O and Ni—W—O systems

Only metallic η oxides were found to exist in these two systems as in the corresponding ternary systems with $\text{Me} = \text{Mn}$. The following lattice constants were measured: $\text{Ni}_3\text{Mo}_3\text{O}$ $a = 10.85\text{—}10.86 \text{ \AA}$, $\text{Ni}_3\text{W}_3\text{O}$ $a = 10.87 \text{ \AA}$. Kuo¹⁰ has recently reported the existence of the η carbide $\text{Ni}_3\text{Mo}_3\text{C}$, while the corresponding $\text{Ni}_3\text{W}_3\text{C}$ ¹¹ carbide was known earlier.

The Cu—Mo—O and Cu—W—O systems

No ternary oxides could be prepared. A careful oxidation only caused the formation of Mo and W oxides.

DISCUSSION

According to the observations of the author the affinity of the transition element used for oxygen under the above mentioned reaction conditions decreases in the sequence Ti—V—Cr—Mn—Fe—Mo—W—Co—Ni—Cu. There is no doubt about the position of Mo before W but the mutual order between

Fe and the pair Mo—W is not quite clear. In any case the differences between the affinities of these three metals for oxygen seem to be small. But it is a remarkable step between Mn and Fe on one side and between W and Co on the other. It is of interest to note that Mo and W only form metallic ternary phases with Mn, Fe, Co, and Ni, *i. e.* metals which are situated close to Mo and W in the above series. η oxides are formed with Mn, Fe, Co, Ni and L'3 oxides with Fe and Co, but evidently not with Mn or Ni. In the non-metallic black compounds $(\text{Cr, Me}'')_2\text{O}_3$ the metals Mo and W seem to have the valence number 3. The degree of affinity for oxygen cannot be a dominating factor for the formation of η oxides, however, as Ti forms such oxides with the metals Mn, Fe, Co, Ni, Cu which have a much smaller affinity for oxygen than Ti. It has even proved to be easier to prepare $\text{Cu}_3\text{Ti}_3\text{O}$ than for instance $\text{Mn}_3\text{Mo}_3\text{O}$.

The oxygen positions in the $\text{Cu}_3\text{Ti}_3\text{O}$ phase could be determined from X-ray data (to be published) confirming the suggestion made by Westgren⁸ that the non-metal atoms in $\text{Fe}_3\text{W}_3\text{C}$ occupy the centres of slightly deformed Me'' octahedra. For isostructural reasons this grouping will, in all probability, include all η carbides and analogous oxides and nitrides. Thus no $\text{Me}'\text{—O}$ contacts occur. In all metallic oxides hitherto prepared — with the exception of Cr_3O , Mo_3O and W_3O — the oxygen atoms are located at the centres of metal atom octahedra. The metals forming metallic Me—O bonds are found among the transition metals in groups IV—VI.

The ratio of the atomic radii of Me'' to Me' lies within the narrow ranges 1.09—1.13 for $\text{Me}'' = \text{Mo, W}$. However, the attainment of this ratio of atomic radii is not itself a sufficient condition for the formation of such carbides¹⁰ and oxides² since there are metals with this ratio which fail to form such η compounds.

In order to find the mutual solubility of η oxides with $\text{Me}' = \text{Mn—Co}$ and $\text{Me}'' = \text{Mo or W}$, different ternary and quarternary alloys with the gross ratio $\text{Me}'/\text{Me}'' = 1$ were prepared and carefully oxidized with steam. It proved difficult to obtain equilibrium, but the obtained results indicated that a homogeneous phase $(\text{Mn, Fe, Co, Ni})_3(\text{Mo, W})_3\text{O}$ most likely exists, where the different kinds of metals can be mixed in all proportions. Attempts to partially replace the nonmetals in $\text{Co}_3\text{W}_3\text{C}$ and $\text{Co}_3\text{W}_3\text{N}$ with O failed and other phases were formed. The question is therefore open if a total mutual solid solubility exists between the η carbides, nitrides and oxides of the metals Mo and W.

SUMMARY

Oxide phases in the systems $\text{Me}'\text{—Me}''\text{—O}$, where $\text{Me}' = \text{Ti—Cu}$ and $\text{Me}'' = \text{Mo and W}$, have been prepared in different ways and investigated by X-ray methods.

Metallic ternary oxide phases of the η carbide structure — $\text{Me}'_3\text{Me}''_3\text{O}$ — and of the L'3 type (the metal atoms distributed at random in a hexagonal close-packed unit cell) — $\text{Me}'\text{Me}''\text{O}$ — have been found to exist with the following combination of atoms: $\text{Me}'_3\text{Me}''_3\text{O}$, $\text{Me}' = \text{Mn, Fe, Co, Ni}$ and $\text{Me}'' = \text{Mo, W}$; $\text{Me}'\text{Me}''\text{O}$, $\text{Me}' = \text{Fe, Co}$ and $\text{Me}'' = \text{Mo, W}$.

Besides these metallic oxides ternary non-metallic oxides have been prepared, *viz.* a $(\text{Cr, Me}'')_2\text{O}_3$ phase ($\text{Me}'' = \text{Mo, W}$) with a rhombohedral structure

related to that of Cr_2O_3 , and a $(\text{Fe}, \text{W})\text{O}_2$ phase with a hexagonal structure closely related to the monoclinic one of WO_2 .

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REFERENCES

1. Ehrlich, P. *Z. anorg. Chem.* **247** (1941) 53.
2. Schönberg, N. *Acta Chem. Scand.* **8** (1954) In print.
3. Seybolt, A. U. and Sumsion, H. T. *J. Metals* **5** (1953) 292.
4. Hägg, G. and Schönberg, N. *Acta Cryst.* (1954) In print.
5. Davey, W. P. *Phys. Rev.* **21** (1923) 716.
6. Goldschmidt, V. M., Barth, T., Lunde, G. and Zachariasen, W. *Geochemische Verteilungsgesetze V*, Oslo (1925).
7. Westgren, A. and Phragmén, G. *Trans. Am. Soc. Steel Treating* **13** (1928) 539.
8. Westgren, A. *Jernkontorets Ann.* **117** (1933) 1.
9. Karlsson, N. *Nature* **168** (1951) 558.
10. Kuo, K. *Acta Metallurgica* **1** (1953) 301.
11. Adelsköld, V., Sandelin, A. and Westgren, A. *Z. anorg. Chem.* **212** (1933) 401.
12. Badger, F. S., and Sweany, W. O. *Am. Soc. Testing Materials*, Symposium on Materials for Gas Turbines, Philadelphia 1946, p. 99.
13. Magnéli, A. *Arkiv Kemi Mineral. Geol. A* **24** (1947) No. 2.

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