On the Existence of Metallic Ternary Oxides $\text{Me}'\text{Me}''\text{O}$ with the Metal Atoms in Hexagonal Close-packing

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During the last three decades, a comprehensive investigation of $\text{Me}-\text{X}$ systems, where Me = a transition metal and X = one of the nonmetals carbon or nitrogen, has revealed the existence of a group of metallic phases with the ideal formula Me_2X . The nonmetal atom X is located at the centre of a metal atom octahedron. The systematic study of these phases was initiated by the work of Hägg^{1,2}. The structure type of the Me_2X phase has been designated by L'3 to indicate the analogy to the A 3 type. Some authors refer to this structure as "Hägg-type". The phases commonly have comparatively broad homogeneity ranges with a highest nonmetal content of 33 atom-%.

No binary oxide phases of the L'3 type have been found to exist, although the maximum solid solubility of oxygen in the α -titanium and α -zirconium lattices seems to correspond to the composition Me_2O .

The present investigation forms part of a study of metallic double-oxides $(\text{Me}', \text{Me}'')\text{O}_x$ among the transition metals, with $\text{Me} = \text{Ti, Zr, Th, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Cu}$. (Cu is here regarded as a transition element.)

The metals used for the preparation of the oxides were of fairly high purity, about 99.5 %. The samples were prepared in three ways:

1. The powdered metals and a suitable oxide of one of the metals were carefully mixed, moulded into brickettes and heated in zirconia crucibles in a high frequency vacuum induction furnace at various temperatures between 1 400° C and 1 800° C.
2. The same mixture of metals and oxide as above was heated in evacuated silica tubes at 1 000° C for times varying between one hour and four weeks.
3. Binary alloys were prepared in a vacuum furnace starting from the powdered metals. The powdered alloys were oxidized by means of steam in the presence of hydrogen in great excess at a temperature of about 700° C.

The best results were obtained with preparation method 1, although the reaction in some cases was of an explosive nature — for instance, between Ti and FeO. The heating of the samples in silica tubes (2) often caused reactions with the inner walls of the tube, especially in the presence of metals in the groups IVa and Va. The samples from method 3 were often heterogeneous.

Table 1. Unit cell dimensions and interatomic distances for the $\text{Me}'\text{Me}''\text{O}$ phases.

Me'	Me''	$c, \text{\AA}$	$a, \text{\AA}$	c/a	$V, \text{\AA}^3$	(Me-Me)dist., $\text{\AA}$ obs.	(Me-Me)dist., $\text{\AA}$ calc.	(O-Me)dist., $\text{\AA}$ obs.	$r_0, \text{\AA}$ calc.
Mo	Fe	4.32	2.75	1.57	28.31	2.72	2.65	1.92	0.60
	Co	4.25	2.74	1.55	27.65	2.70	2.64	1.91	0.59
W	Fe	4.31	2.75	1.57	28.23	2.71	2.67	1.92	0.58
	Co	4.29	2.75	1.56	27.96	2.71	2.66	1.91	0.58
Re	Ti	4.61	2.85	1.62	32.41	2.84	2.84	2.01	0.59
	V	4.46	2.76	1.62	29.45	2.75	2.73	1.95	0.58
	Cr	4.45	2.75	1.62	29.20	2.74	2.67	1.94	0.61
	Mn	4.38	2.72	1.61	28.05	2.71	2.64	1.91	0.59
	Fe	4.37	2.71	1.61	27.26	2.70	2.63	1.91	0.59
	Co	4.32	2.69	1.61	27.05	2.68	2.62	1.89	0.58
"Ti ₂ O"		4.81	2.96	1.63	36.50	2.96	2.98	2.01	0.60
"Zr ₂ O"		5.24	3.27	1.61	48.45	3.25	3.20	2.30	0.70

For the X-ray analysis, cameras of the Guinier type constructed at this institute were used. The cameras incorporated either a bent quartz monochromator or an aluminium monochromator with double curvature.

Besides other ternary oxides, a series of $(\text{Me}', \text{Me}'')\text{O}_x$ phases were obtained with the metal atoms randomly distributed in a hexagonal close-packed arrangement and the Me'/Me'' ratio close to unity. The phase analysis indicated that the value of x can vary (to some degree) within the approximate limits $0.2 < x < 0.5$. The value of x never exceeded 0.5. By analogy with the carbides and nitrides of the L'3 type the ideal formula may be written $\text{Me}'\text{Me}''\text{O}$. The following combinations of transition metals were found to exist:

$\text{Me}' = \text{Mo} - \text{Me}'' = \text{Fe}, \text{Co}$

$\text{Me}' = \text{W} - \text{Me}'' = \text{Fe}, \text{Co}$

$\text{Me}' = \text{Re} - \text{Me}'' = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$

For $\text{Me}' = \text{Re}$ some of the phases probably exist with $x = 0$, i.e. without any oxygen in the lattice. This is definitely not the case for the phases containing Mo or W. In the four ternary systems $\text{Mo}-\text{Fe}-\text{O}$, $\text{Mo}-\text{Co}-\text{O}$, $\text{W}-\text{Fe}-\text{O}$, and $\text{W}-\text{Co}-\text{O}$, phases of the "high speed steel carbide" (η -carbide) structure with the formula $\text{Me}_3'\text{Me}_3''\text{O}$ have been prepared, i.e. with an oxygen content of about 14 atom-%. These oxides are isomorphous with the compounds $\text{Me}_3\text{Ti}_3\text{O}$, where $\text{Me} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ earlier reported by the present author⁴. A cautious oxidation of the oxides of the η -carbide type containing Mo or W caused the formation of oxides of the L'3 type. This proves that the last-mentioned phases only exist with a higher oxygen content than 14 atom-%. An increase of the unit cell volume per metal atom further accentuates this fact.

In a few cases weak extra reflections appeared in the powder photographs of the $\text{Me}'\text{Me}''\text{O}$ phases. These extra reflections do not necessitate an enlargement of the unit cell. They indicate a low degree of order in the metal lattice.

The calculation of $p|F|^2$ values for ordered oxygen atoms shows namely, that the resulting extra lines in this case should be hardly visible in the photographs for $\text{Me}'' = \text{Mo}$ and undetectable for $\text{Me}'' = \text{W}$ and Re .

The unit cell dimensions and interatomic distances are listed in Table 1. As indicated by the variation of the lattice constants — commonly of the order 0.1 % — the homogeneity ranges are comparatively small. The axial lengths reported are mean values. The observed mean interatomic distances are compared with those given by Pauling for 12-coordination of atoms⁵. The last column in Table 1 gives the calculated atomic radius for the oxygen atom. It is seen that the deviations from $r_0 = 0.60 \text{ \AA}$ is very small. The data obtained for the α -Ti and α -Zr phases with interstitially dissolved oxygen in equilibrium with the TiO and ZrO phases respectively have also been included in the table.

SUMMARY

Metallic double-oxides including two transition elements (Me' , Me'') have been prepared in various ways and investigated by X-ray methods.

$\text{Me}'\text{Me}''\text{O}_x$ phases with the metal atoms in hexagonal close-packing, where $0.4 < x < 1$, have been found to exist for the following combination of atoms:

$\text{Me}' = \text{Mo} - \text{Me}'' = \text{Fe, Co}$

$\text{Me}' = \text{W} - \text{Me}'' = \text{Fe, Co}$

$\text{Me}' = \text{Re} - \text{Me}'' = \text{Ti, V, Cr, Mn, Fe, Co}$

For the $\text{Me}' = \text{Re}$ some of the phases probably exist with $x = 0$, *i.e.* without any oxygen in the lattice. This is definitely not the case for the phases containing Mo or W.

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