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PREPARATION OF $V_aM_{2-a}O_4$ (M = Nb, Ta; $1 \geq a \geq 0.2$) WITH DIFFERENT OXYGEN CONTENTS

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This paper describes the thermal behaviour of various oxides of pentavalent V and Nb or Ta in different dynamic hydrogen atmospheres. Previous studies of the phases obtained by heating mixtures of V_2O_5 and M_2O_5 (M = Nb, Ta) in air lead to (i) preparation of $VTaO_5$ from both oxides for the first time, (ii) proof of the existence of the solid-solutions $VM_mO_{5/2(m+1)}$, and (iii) proof that the materials described as $NbVO_5$ and β-$TaVO_5$ are really mixtures of VM_9O_{25} and V_2O_5. Reduction of VMO_5 gives monophasic rutile-type VMO_4 from 650°C. Reduction $VM_2O_{7.5}$, $V_3M_{17}O_{50}$ and VM_9O_{25} at 1000°C leads to monophase non-stoichiometric $V_aM_{2-a}O_y$ only for M = Nb.

Keywords: solid-solutions, V and Nb or Ta oxides

Introduction

Although several authors [1–3] have paid special attention to the oxides VMO_5, when we tried to prepare these oxides various results made it necessary to repeat an early investigation [1] in order to study the phases produced by heating mixtures of V_2O_5 and M_2O_5 in air. For this reason the present investigation had two aims: to elucidate the nature of these phases, and to study their reduction carried out in several dynamic hydrogen atmospheres.

To date $VNbO_5$ has been obtained [4] by sol–gel methods and $VTaO_5$ h as only been synthesized [3] by solid-state reaction from a mixture of V_2O_5 and $H_2Ta_2O_6 \cdot H_2O$. For intermediate members of the isomorphous series $VM_mO_{5/2(m+1)}$, two have been described previously [5, 6]. The rutile-type compound $VNbO_4$, with the metals in a lower oxidation state, has been known for some time [7] but this was prepared from VO_2 and NbO_2.

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Experimental

We prepared mixtures of reagent grade V_2O_5 and M_2O_5 (M = Nb, Ta) with different V:M molar ratios. These mixtures were ground, weighed and heated in air at increasing temperatures. After each thermal treatment, the products were weighed, re-ground and identified by X-ray powder diffraction. $VTaO_5$ was prepared by heating mixtures with V:Ta molar ratio equal to 1:1 at 640°C for 20 hours, and heating again at 740°C for 20 hours. The Nb-containing samples with V:M molar ratios of 1:2, 1:5.6 and 1:9 were heated at 640°C for 20 hours, 740°C for 20 hours and 750°C for 10 hours; those with M = Ta, at 640°C for 20 hours, 740°C for 20 hours, 750°C for 20 hours, and three times at 900°C for 6 hours.

The X-ray powder diffraction study was performed using a Siemens Kristalloflex 810 computer-controlled diffractometer, a D-500 goniometer provided with 2θ-compensating slit and graphite monochromator, and $CuK_{\alpha 1}$ radiation with λ = 1.5405981 Å. Patterns for identification purposes were made at a scanning rate of 2° 2θ min^{-1}. The more accurate *d*-spacing measurements were performed at 0.1° 2θ min^{-1} using tungsten as internal standard.

Thermal investigation of the various oxides of vanadium and niobium or tantalum was carried out in two kinds of dynamic hydrogen atmospheres: using pure hydrogen or a mixture of 5% hydrogen and 95% argon. In both cases the flow was 200 $ml\cdot min^{-1}$. A Mettler TA 3000 system with a heating rate of 300 $deg\cdot h^{-1}$ was used.

Results and discussion

Thermal stability of $VTaO_5$

Investigation of the phases produced by heating mixtures of V_2O_5 and M_2O_5 in air allowed definition of the production route for $VTaO_5$ by solid-state reaction of V_2O_5 and Ta_2O_5 in molar ratio 1:1. $VTaO_5$ crystallizes in the orthorhombic system with a = 11.860(4) Å, b = 5.506(4) Å, and c = 6.924(3) Å, and is stable up to 900°C; however if heated at this temperature for long periods, for instance 20 hours, it transforms into an ochre-coloured powder whose X-ray powder pattern coincides with that assigned [1, 2] erroneously to a non-existent β-$VTaO_5$, stable above 885°C. We have verified that this is a mixture of VTa_9O_{25} [8] and V_2O_5. We have shown that the compound described [1] as $VNbO_5$ is quite possibly a mixture of VNb_9O_{25} [8] and V_2O_5.

The TG curve of $VTaO_5$ in air to 1000°C is a straight line, so the transformation of $VTaO_5$ to the material described as β-$TaVO_5$ occurs without weight loss according to the equation

$$9VTaO_5 \rightarrow 4V_2O_5 + VTa_9O_{25}$$

Characterization of the isomorphous series $VM_mO_{5/2(m+1)}$

In these two isomorphous series, materials with compositions $VNb_2O_{7.5}$, $VTa_2O_{7.5}$, $V_3Ta_{17}O_{50}$ and VTa_9O_{25} had not been previously prepared [9]. The six materials obtained from the general composition $VM_mO_{5/2(m+1)}$ crystallize in the tetragonal system. Unit-cell parameters and correlation factors given in Table 1 show that vanadium and tantalum form a tetragonal solid solution ranging from Ta:V = 2 to Ta:V = 9. Similar behaviour is shown by the vanadium and niobium samples.

Table 1 Unit-cell parameters and correlation r factors for tetragonal $VTa_mO_{5/2(m+1)}$

m	a /Å	c /Å	V /Å^3
2	15.6784 (7)	3.8253 (6)	940.3 (1)
5.6	15.6808 (9)	3.8260 (9)	940.8 (2)
9	15.684 (1)	3.828 (1)	941.7 (3)
	$r_a = 0.994$	$r_c = 0.956$	$r_V = 0.982$

Thermal study

When a hydrogen stream was used for reducing VMO_5, reduction was complete at about 650°C, but the sample was kept at that temperature for 1 hour in order to ensure complete reaction. The reduction product was a black powder with an oxygen content of 4.3 for the niobium compound and very close to 4 for that of tantalum. The X-ray powder patterns of both residual were very similar and corresponded to the rutile-type compound VMO_4.

We also performed reduction of the compounds described as $VNbO_5$ and β-$VTaO_5$, which constitutes additional proof that these materials are not pure compounds but mixtures.

Figure 1 shows TG curves corresponding to reduction of $VNbO_5$ (curve *a*), $VTaO_5$ (curve *b*), and the 'compound' β-$TaVO_5$ (curve *c*) carried out using pure hydrogen. The X-ray pattern of the residuum at 1000°C of curve *c* corresponds to a mixture of $VTaO_4$ and different vanadium oxides with valency lower than 5. This result confirms that the material described as β-$VTaO_5$ is a mixture. Reduction of the compound formulated as $VNbO_5$ leads to a similar conclusion: it is actually mixture of VNb_9O_{25} and V_2O_5.

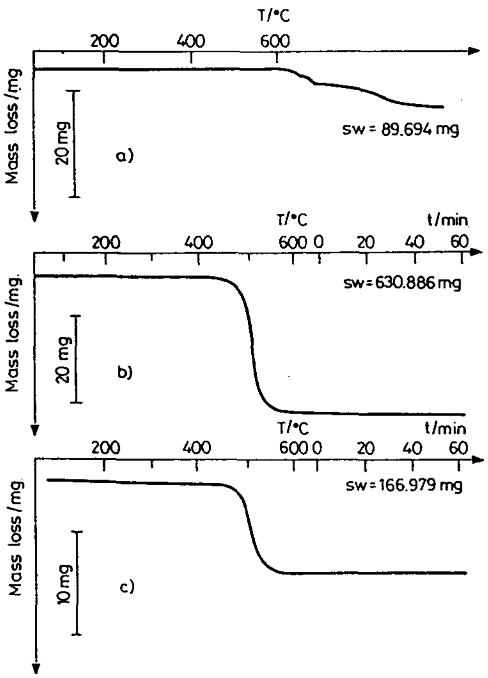

Fig. 1 TG curves of $VNbO_5$, $VTaO_5$ and the 'compound' β-$VTaO_5$ in hydrogen stream

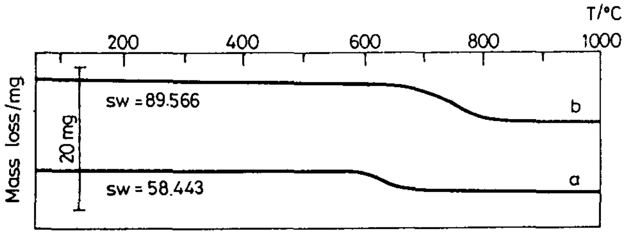

Fig. 2 TG curves for $VNbO_5$ and $VTaO_5$ in flowing hydrogen (5%) and argon (95%)

When the reduction of VMO_5 was carried out using a mixture of hydrogen and argon, the compounds VMO_4 were obtained with the same oxygen contents as those obtained using a hydrogen stream. In these conditions it was necessary to reach a higher temperature in order to assure complete reduction. Figure 2 shows the TG curves to 1000°C for $VNbO_5$ (curve *a*) and $VTaO_5$ (curve *b*).

Reduction of the tetragonal solid solutions was also studied. Figure 3 shows the TG curves of six members of the series $VM_mO_{5/2(m+1)}$ carried out using a

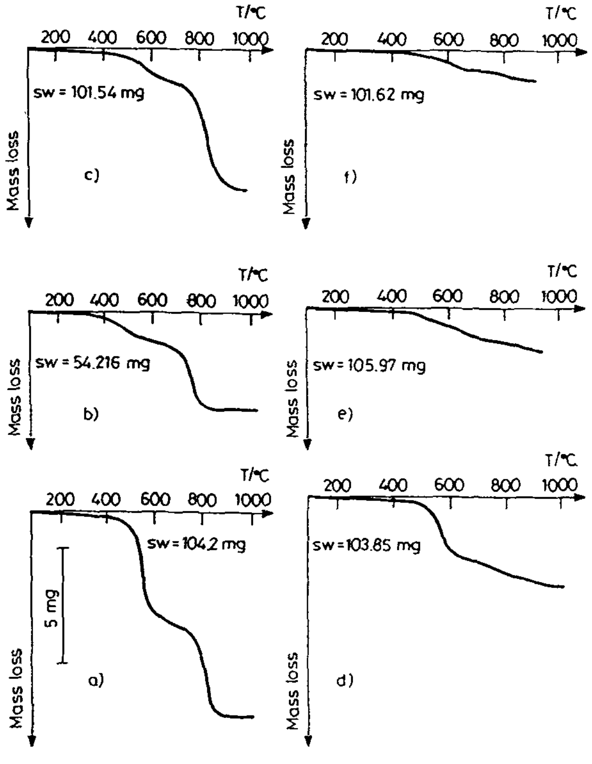

Fig. 3 TG curves for the series $VM_mO_{5/2(m+1)}$ in hydrogen stream

hydrogen stream. Curves *a*, *b* and *c* allow us to establish that the reduction of $VNb_2O_{7.5}$, $VNb_{17}O_{50}$ and VNb_9O_{25} may be described by the equations

$$VNb_2O_{7.5} \rightarrow 3(V_{0.33}Nb_{0.67}O_{1.87}) + 0.95\ O_2$$

$$V_3Nb_{17}O_{50} \rightarrow 20(V_{0.15}Nb_{0.85}O_{1.89}) + 6.10\ O_2$$

$$VNb_9O_{25} \rightarrow 10(V_{0.1}Nb_{0.9}O_{1.96}) + 2.70\ O_2$$

X-ray analysis of samples taken at 1000°C from curves *a*, *b* and *c*, shows that non-stoichiometric phases are obtained with compositions $V_{0.67}Nb_{1.33}O_{3.74}$, $V_{0.30}Nb_{1.70}O_{3.78}$ and $V_{0.2}Nb_{1.8}O_{3.92}$, respectively.

Curves *d*, *e* and *f* correspond to the reduction of $VTa_2O_{7.5}$, $V_3Ta_{17}O_{50}$ and VTa_9O_{25}. As expected, X-ray diffraction patterns of samples taken at 1000°C from these curves show that the rutile-type phase $V_aTa_{2-a}O_y$ is mixed with the starting material and very small amounts Ta_2O_5. This suggests that these Ta-containing materials are reduced at higher temperatures than those of Nb.

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Zusammenfassung – Es wird das thermische Verhalten verschiedener Oxide von pentavalentem V und Nb oder Ta in verschiedenen dynamischen Wasser-stoffatmosphären beschrieben. Frühere Untersuchungen der durch Erhitzen eines Gemisches aus V_2O_5 und M_2O_5 (M = Nb, Ta) in Luft erhaltenen Phasen führten (i) zur erstmaligen Darstellung von $VTaO_5$ aus beiden Oxiden, (ii) zum Nachweis der Existenz des Mischkristalles $VM_mO_{5/2(m+1)}$ und (iii) zum Nachweis, daß die als $NbVO_5$ und als ß-$TaVO_5$ beschriebenen Substanzen in Wirklichkeit Gemische aus VM_9O_{25} und V_2O_5 sind. Die Reduktion von VMO_5 ergibt ab 650C eine Monophase VMO_4 vom Rutil-Typ. Die Reduktion von $VM_2O_{7.5}$, $V_3M_{17}O_{50}$ und VM_9O_{25} bei 1000C führt nur für M = Nb zu einer nichtstöchiometrischen Monophase $V_aM_{2-a}O_y$.