Processes in the Reaction of Y_2O_3 with WO_3

Kiyoshi KURIBAYASHI and Toshiyuki SATA

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received April 2, 1977)

The processes of the solid state reaction of Y_2O_3 with WO_3 were studied for samples mixed in the molar ratios of $Y_2O_3 : WO_3 = 1 : 3$, $1 : 1$, $7 : 4$, $5 : 2$, and $3 : 1$. It was found that all the reactions except $Y_2O_3 : WO_3 = 5 : 2$ from the powders of both Y_2O_3 and WO_3 in air proceeded according to the following order step reactions: $Y_2O_3 \cdot 3WO_3 \rightarrow Y_2O_3 \cdot WO_3 \rightarrow 7Y_2O_3 \cdot 4WO_3 \rightarrow 5Y_2O_3 \cdot 2WO_3$ and $5Y_2O_3 \cdot 2WO_3 \rightarrow 3Y_2O_3 \cdot WO_3$, with temperatures rising from 600 to 1300 °C and with an unknown compound, X, always first formed below 700 °C. In a reaction couple in contact with both Y_2O_3 and WO_3 pellets, WO_3 components preferentially diffused to the Y_2O_3 side to form $Y_2O_3 \cdot 3WO_3$ (orthorhombic form) on the boundary between them at 1000 °C.

The compounds formed in the reaction of the sesquioxides of the rare earth elements (R_2O_3) with WO_3 are attracting the attention of research workers because of the possibility of using them as engineering materials: refractory materials, dielectrics, laser materials, and luminescents materials. They are also interesting from a crystallographical point of view and from the point of view of reaction kinetics.

H. J. Borchardt[1] studied a phase relation in the Y_2O_3–WO_3 system and reported that there were six compounds: $Y_2O_3 \cdot 3WO_3$, $Y_2O_3 \cdot WO_3$, $3Y_2O_3 \cdot 2WO_3$ (metastable phase), $15Y_2O_3 \cdot 8WO_3$, $9Y_2O_3 \cdot 4WO_3$, and $3Y_2O_3 \cdot WO_3$. Recently, G. H. McCarthy *et al.*[2] reported that five compounds existed in the system: $Y_2O_3 \cdot 3WO_3$ (YW_3), $Y_2O_3 \cdot WO_3$(YW), $7Y_2O_3 \cdot 4WO_3$-(Y_7W_4), $5Y_2O_3 \cdot 2WO_3$(Y_5W_2), and $3Y_2O_3 \cdot WO_3$(Y_3W). However, the Y_2O_3-rich region of the system has not yet been made clear.

In the present study, the processes of the solid state reaction between Y_2O_3 and WO_3 were studied. Also, we tried to determine what the diffusion component was through an interface where the two oxides came in contact using an electron-probe microanalyzer (EPMA).

Experimental

Both dried Y_2O_3(Rare-Metallic Co., 99.99%) and WO_3 (Mitsuwa Chemical Co., 99.9%), calcined at 800 °C for 3h, were weighed in the appropriate oxide ratio and were mixed thoroughly in an agate mortar. These oxide mixtures were then pressed into pellets at 800 kg cm^{-2}. The pellets were then heated in air on an alumina boat for 48 h at temperatures from 600 °C up to 1300 °C in a mullite tube in a silicon carbide furnace. The temperature was controlled within ±10 °C. After heating, the products were identified by the X-ray powder diffraction methods.

Y_2O_3 was pressed into a pellet at 3200 kg cm^{-2} and sintered in air at 1400 °C for 48 h; the apparent porosity of the pellet was 19%. The surface of the pellet was polished with diamond paste. A 0.2 mmϕ platinum wire was fixed as a marker on the Y_2O_3 pellet and was then pressed into a larger pellet, with WO_3 powder covering the pellet, at 3200 kg cm^{-2}. It was heated on an alumina boat in air for 72 h at 1000 °C. After cooling, the pellet was cut off perpendicular to the interface between the Y_2O_3 and WO_3 layers, as is shown in Fig. 1a. The cut surface was polished and measured by means of an EPMA.

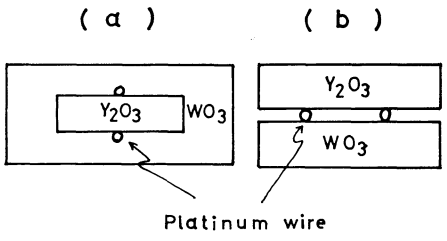

Fig. 1. Schematic diagrams of specimen to study diffusion components.

Each portion of Y_2O_3 or WO_3 was pressed into a pellet at 3200 kg cm^{-2}. The Y_2O_3 pellet was sintered at 1400 °C, while the WO_3 was sintered at 1000 °C for 48 h. After cooling, both the pellets were placed with a 0.2 mmϕ platinum wire sandwiched between, in order to give a clearance of 0.2 mm between them, as is shown in Fig. 1b. The above sandwich-type specimen, wrapped up by a platinum plate, was covered with WO_3 powder in order to confirm the occurrence of a reaction of solid-state Y_2O_3 with WO_3 vapor and was heated on an alumina boat in air at 1000 °C for 72 h.

Results

The relative amounts of phases present in the products after Y_2O_3–WO_3 reactions for 48 h in air at each temperature are shown in Fig. 2a—e. The relative amounts were obtained from the intensities of the peaks on the X-ray diffraction pattern from each compound. It was found that all the reactions except $Y_2O_3 : WO_3 = 5 : 2$ from both Y_2O_3 and WO_3 in air proceeded according to the following order: $YW_3 \rightarrow YW \rightarrow Y_7W_4 \rightarrow Y_5W_2$ and $Y_5W_2 \rightarrow Y_3W$, with temperatures increasing from 600 °C up to 1300 °C, though for the reaction of $5Y_2O_3 + 2WO_3$, Y_3W was formed by the reaction of Y_2O_3 with a part of the Y_7W_4 and the reaction of $6(Y_3W) + Y_7W_4 \rightarrow 5(Y_5W_2)$ yielded the Y_5W_2 compound. The unknown compound, X, was first formed for all the reactions; its X-ray diffraction diagram, shown in Table 1, has not been indexed. Oxide mixtures weighed in the molar ratios of $Y_2O_3 : WO_3 = 1 : 2$, $1 : 3$, or $1 : 4$ were heated in air at temperatures from 600 °C up to 800 °C for 5 days in order that Compound X could be studied in detail. The pellets were reground twice during the heating schedule and then pelletized again in order to insure homogeneity. The products are shown in Table 2. It was impossible to obtain Compound X alone for each composition because of the incomplete reactions. The same results were obtained from 10 days' heating.

A microscopical photograph of the EPMA specimen

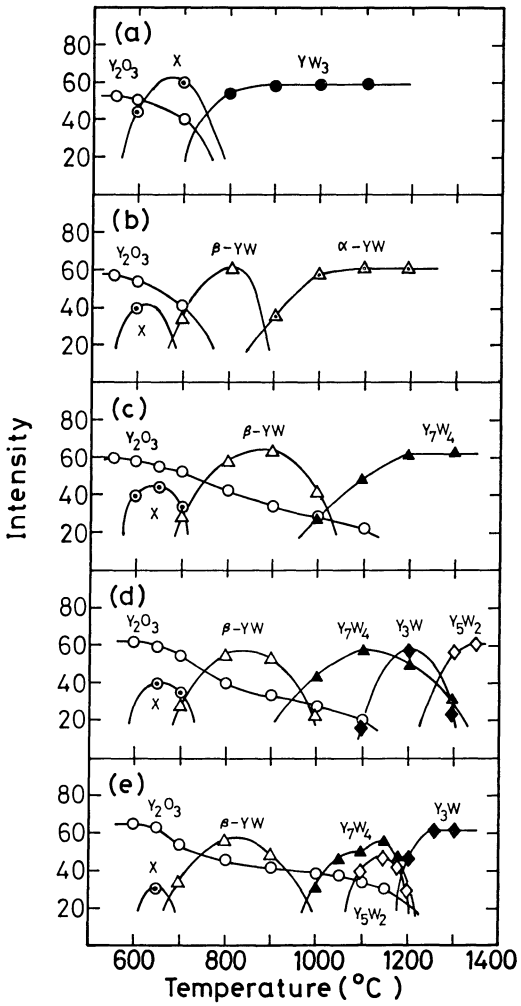

Fig. 2. Relative amounts of phases present in the products from Y_2O_3–WO_3 reactions for 48 h in air at each temperature. (a) Y_2O_3–$3WO_3$, (b) Y_2O_3–WO_3, (c) $7Y_2O_3$–$4WO_3$, (d) $5Y_2O_3$–$2WO_3$, (e) $3Y_2O_3$–WO_3. Y_2O_3, (662), (○); X, 2θ=18.8, (⊙); YW_3, 2θ=20.3, (●); α-YW, 2θ=33.6, (△); β-YW, (112), (△); Y_7W_4, (003), (▲); Y_5W_2, (113), (◇); Y_3W, (003), (◆).

(Fig. 1a) and the results of the EPMA measuremnts are shown in Fig. 3. The WO_3 layer was detached from the reaction layer because of a difference in thermal expansion between WO_3 and the reaction product. A reaction layer 120μm thick was produced as a single layer in the Y_2O_3 layer. The diffusion of Y_2O_3 component to WO_3 side was negligible. The reaction layer was found to be YW_3(orthorhombic form) using the X-ray powder diffraction methods and the EPMA.

On the other hand, no reaction layer was found by the X-ray powder diffraction methods or microscopic observation of the specimen shown in Fig. 1b and heated for 72h at 1000 °C.

Discussion

The Sample Mixed in the Ratio of Y_2O_3 : WO_3=1 : 3. Compound X began to form at about 600 °C, and YW_3 (orthorhombic from) was produced above 800 °C. It

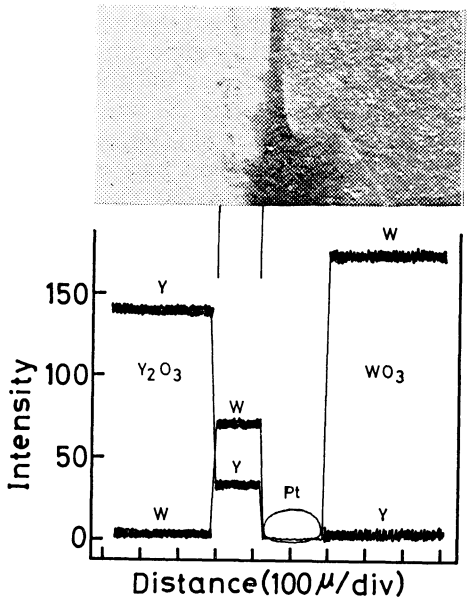

Fig. 3. A microscopical photograph and a result of a EPMA measurement for a reaction couple contacted both Y_2O_3 and WO_3 pellets.

Table 1. X-Ray powder data for compound X

Line No.	d	I/I_0
1	6.0619	5
2	5.3358	20
3	4.7111	80
4	3.5319	15
5	3.1475	90
6	3.0024	100
7	2.8289	30
8	2.5902	50
9	2.3272	15
10	2.2097	10
11	1.9087	60
12	1.9049	60
13	1.8974	30
14	1.6876	20

Table 2. Products from Y_2O_3–WO_3 reaction heated in air for 5 days

Temp	$Y_2O_3+2WO_3$	$Y_2O_3+3WO_3$	Y_2O_3+4WO
600 °C	$X+Y_2O_3$	$X+Y_2O_3+WO_3$	$X+WO_3+Y_2O_3$[a]
700 °C	$X+Y_2O_3$	$X+Y_2O_3+WO_3$	$X+WO_3+Y_2O_3$[a]
800 °C	$YW_3+Y_2O_3$	YW_3	YW_3+WO_3

a) Trace of Y_2O_3.

was impossible to obtain Compound X alone because of the slow reaction rate at low temperatures, as is shown in Table 2; *i.e.*, oxide mixtures with this bulk composition, when subjected to the usual heat treatment at 600 or 700 °C, yielded products which consisted of Compound X and unreacted Y_2O_3 and WO_3. The phase changes for $R_2O_3 \cdot 3WO_3$ (R=Dy and Ho) were reported by V. E. Plyuschev and V. M. Amosov[3] and those for R=La—Dy, by K. Nassau *et al.*[4] M. Yoshimura *et al.*[5–7] synthesized $2R_2O_3 \cdot 9WO_3$ (R=La,

Ce, Pr, and Nd) and pointed out that rare earths which are heavier than Sm would be too small to form this type of compound. Considering the above reports and the present results, Compound X can be assumed to be a high-temperature form of YW_3 or a compound near to YW_3. This compound may exist as a metastable phase between 600 and 700 °C.

The Sample Mixed in the Ratio of Y_2O_3 : WO_3=1 : 1. Compound X began to form at about 600 °C, and the Y_3W_2 (metastable phase) reported by H. J. Borchardt[1] was yielded about 700 °C. Recently, M. Yoshimura *et al.*[8] reported that this metastable phase was a high-temperature form(β-phase) of YW plus Y_2O_3. A low-temperature form(α-phase) of YW was produced above 900 °C through the process of Compound X→β-YW→α-YW. YW_3 (orthorhombic form) was not observed in this process.

The Sample Mixed in the Ratio of Y_2O_3 : WO_3=7 : 4. The compound of Y_7W_4 was produced above 960 °C through the process of Compound X→β-YW→Y_7W_4. YW_3 and α-YW(low-temperature form) were not formed, as is the case of the sample mixed in the ratio of Y_2O_3 : WO_3=1 : 1. Similar results were obtained for the formation of Y_5W_2 and Y_3W.

The Sample Mixed in the Ratio of Y_2O_3 : WO_3=5 : 2. After passing through the process of Compound X→β-YW→Y_7W_4, the reaction of Y_2O_3 with a part of Y_7W_4 yielded Y_3W. The Y_5W_2 compound was produced by the reaction of Y_7W_4 with Y_3W at temperatures higher than 1300 °C.

G. J. McCarthy *et al.*[2] reported that $5R_2O_3 \cdot 2WO_3$ was found only for the rare earths, R=Gd—Ho and Y. The reaction products from mixtures with their bulk compositions, after usual heat treatment at 1400 °C, consisted of $3R_2O_3 \cdot WO_3$, plus $7R_2O_3 \cdot 4WO_3$ for other rare earths. $5R_2O_3 \cdot 2WO_3$ may be also yielded by heating at temperatures higher than 1400 °C for the other rare earths, because the reactions proceeding at 1400 °C for them correspond to that of the mixture of $5Y_2O_3$ and $2WO_3$ heated at 1200 °C.

The Sample Mixed in the Ratio of Y_2O_3 : WO_3=3 : 1. After passing through the process of Compound X→β-YW→Y_7W_4, the compound of Y_3W(low-temperature form) was produced by a reaction of Y_2O_3 with Y_7W_4 and Y_5W_2 above 1200 °C. The high-temperature form of Y_3W was not yielded before the production of the low-temperature form from this oxide mixture. It is different from the other samples because the reaction temperature is sufficiently high to enhance the mobilities of the reactant ions, and transition temperature of Y_3W is about 1800 °C too high compared to this reaction temperature.

Reaction of Pellets of Y_2O_3 and WO_3. Considering that the vapor pressure of WO_3 was as low as 10^{-5} Torr[9] at 1000 °C and that the reaction layer did not form in the specimen shown in Fig. 1b, it can be said that the solid state reaction of pellets of both Y_2O_3 and WO_3 occurred in the specimen shown in Fig. 1a. Flor Giorgio *et al.*[10] reported that the $WO_3+SrCO_3 \rightarrow SrWO_4+CO_2$ solid state reaction was controlled by the counterdiffusion of cations involving W^{6+} and Sr^{2+}. E. V. Tkachenko *et al.*[11] reported that the elements of the tungsten sublattice in $CuWO_4$ and Cr_3WO_6 had a higher mobility than that of the copper sublattice. It is possible to consider the diffusion of W^{6+}, so W^{6+} and O^{2-} may be preferentially diffused to the Y_2O_3 side in the reaction of the pellets of both Y_2O_3 and WO_3. The reaction process of Y_2O_3 with WO_3 is similar to that of boron with tungsten metal reported earlier by one of the present authors;[12] the reaction from both BN and W proceeded thus: $WB_4 \rightarrow WB_2 \rightarrow WB$ and $WB \rightarrow W_3B$ with an increase in the temperature because the diffusibility of B is higher than that of W. Such a reaction is due to the significant difference in mobilities between the reactant ions. The diffusion species, W^{6+}, or any W–O complex ions must be confirmed by a more detailed examination of the reaction kinetics.

Conclusion

(1) All the reactions of the powders of both Y_2O_3 and WO_3 in air proceeded according step-by-step in the following order: $YW_3 \rightarrow YW \rightarrow Y_7W_4 \rightarrow Y_5W_2$ and $Y_5W_2 \rightarrow Y_3W$ with the elevation of the temperature from 600 °C up to 1300 °C, and an unknown compound, X, was always first formed below 700 °C.

(2) In a reaction couple bringing Y_2O_3 and WO_3 pellets in contact with each other, WO_3 components preferentially diffused to the Y_2O_3 side to form YW_3 (orthorhombic form) on the boundary between them at 1000 °C.

The authors wish to thank Dr. Masahiro Yoshimura of this laboratory for his helpful advice and discussions.

References

1) H. J. Borchardt, *Inorg. Chem.*, **2**, 170 (1963).
2) G. J. McCarthy, R. D. Fisher, and G. C. Johonon, NBS special publication, **364**, 397 (1972).
3) V. E. Plyuschev and V. M., Amosov *Dokl. Akad. Nauk SSSR*, **157**, 131 (1964).
4) K. Nassau, H. J. Levinstein, and G. M. Loiacono, *J. Phys. Chem. Solids*, **26**, 1805 (1965).
5) M. Yoshimura, T. Sata, and T. Nakamura, *Nippon Kagaku Kaishi*, **6**, 914 (9170).
6) M. Yoshimura, F. Sibieude, A. Rouanet, and M. Foex, *J. Solid State Chem.*, **16**, 219 (1976)
7) M. Yoshimura, H. Morikawa, and M. Miyake, *Mater. Res. Bull.*, **10**, 1221 (1975).
8) M. Yoshimura, F. Sibieude, A. Rouanet, and M. Foex, *Rev. Int. Htes. Temp. et Refract*, **12**, 215 (1975).
9) J. L. Margrave, "The Characterization of High-Temperature Vapors," John Wiley & Sons, New York (1967), p. 497.
10) F. Giorgio, M. Vincenzo, and R. Riccardo, *Z. Naturforsch., Teil A*, **29**, (3) 503 (1974).
11) E. V. Tkachenko, T. F. Telnykh, V. M. Zhukovskii, and A. S. Zhukovskaya, *Russ. J. Phys. Chem.*, **50**, 969 (1976).
12) T. Sata and T. Urano, *Yogyo Kyokai Shi*, **78**, 21 (1970).