THERMAL DECOMPOSITION OF THREE COMMERCIAL POLYPHASE AMMONIUM MOLYBDATE①

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ABSTRACT DTA/TGA and XRD were employed to study the thermal decomposition of three commercial polyphase ammonium molybdate mixtures. A series of intermediate phases of ammonium molybdates, in which the content of molybdenum increases with the raise of temperature, were identified during the course of heating. The main decomposition reactions occurred in steps as follows: (1) at 110 ℃, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ decomposed into $(NH_4)_4Mo_5O_{17}$; (2) at 220 ℃, $(NH_4)_4Mo_5O_{17}$ decomposed into $(NH_4)_2Mo_4O_{13}$; (3) at 290 ℃, $(NH_4)_2Mo_4O_{13}$ or β-$(NH_4)_2Mo_4O_{13}$ decomposed into MoO_3.

Key words ammonium molybdate thermal decomposition metallic molybdenum

1 INTRODUCTION

The starting material for the production of metallic molybdenum is usually ammonium molybdate.

As the preparation process of monophase ammonium molybdate is difficult to control, polyphase ammonium molybdate mixtures are obtained in most cases. In this paper, the thermal decomposition of three commercial ammonium molybdate mixtures was studied by XRD and DTA/TGA in order to get a full understanding on the effect of the starting material on the calcination product MoO_3. The compositions of the three mixtures were[1] AM-1: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (small amount) + $(NH_4)_4Mo_5O_{17}$ + $(NH_4)_2Mo_4O_{13}$ (small amount) + β-$(NH_4)_2Mo_4O_{13}$; AM-2: $(NH_4)_2Mo_4O_{13}$ + β-$(NH_4)_2Mo_4O_{13}$ + $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$ (small amount) and AM-3: $(NH_4)_2Mo_4O_{13}$ + β-$(NH_4)_2Mo_4O_{13}$ + $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$.

2 RESULTS AND DISCUSSIONS

2.1 DT/TG *Analyses*

Differential thermal and thermogravimetric analyses were carried out in open air on a Dupont 9 900 thermometer from room temperature (13 ℃) to 450 ℃ at a rate of 5 ℃/min. The DTA/TGA curves are shown in Fig. 1.

2.2 XRD *Analysis*

The ammonium molybdate mixtures were heated in open air with a heating rate of 10 ℃/min. The phase developments during the course of heating were examined with a 3014 X-ray diffractometer at a series of increasing temperatures. Phases identified in the mixtures from the XRD patterns are listed in Table 1~ 3 where L, S and T represent large, small and tiny amounts of phases, respectively.

2.3 *Thermal Decomposition*

Studies[2-5] have been done about the thermal decomposition of monophase ammonium molybdates. When heated, NH_3 and H_2O are given off and a series of intermediate phases of higher content of molybdenum are formed with MoO_3 as the final product. Some of the decomposition reactions[2, 3] are:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \xrightarrow{\sim 130\ ℃} (NH_4)_4Mo_5O_{17} + NH_3\uparrow + H_2O\uparrow \quad (1)$$

$$(NH_4)_4Mo_5O_{17} \xrightarrow{\sim 245\ ℃} (NH_4)_2Mo_4O_{13} +$$

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Fig. 1 DTA/TGA curves of AM-1(a), AM-2(b) and AM-3(c)

Table 1 Phase composition of AM-1 at different temperatures

t / ℃	13	110	200	240	300	350	400	450
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	S	S						
$(NH_4)_4Mo_5O_{17}$	L	L	L	T	T			
$(NH_4)_2Mo_4O_{13}$	S	S	S	L	L	T		
β-$(NH_4)_2Mo_4O_{13}$	L	L	L	L	L	T		
$(NH_4)_2Mo_{14}O_{43}$					L			
$(NH_4)_2Mo_{22}O_{67}$						L	T	
MoO_3					S	L	L	L

Table 2 Phase composition of AM-2 at different temperatures

t / ℃	13	100	200	300	350	400	450
$(NH_4)_2Mo_4O_{13}\cdot 2H_2O$	S	S	S	S			
$(NH_4)_2Mo_4O_{13}$	L	L	L	L	T		
β-$(NH_4)_2Mo_4O_{13}$	L	L	L	L	T		
$(NH_4)_2Mo_{14}O_{43}$				S			
$(NH_4)_2Mo_{22}O_{67}$					L	T	
MoO_3				S	L	L	L

Table 3 Phase composition of AM-3 at different temperatures

t / ℃	13	150	250	300	350	375	400	425	450
$(NH_4)_2Mo_4O_{13}\cdot 2H_2O$	L	L	L	S					
$(NH_4)_2Mo_4O_{13}$	L	L	L	L	T				
β-$(NH_4)_2Mo_4O_{13}$	L	L	L	L	T	T			
$(NH_4)_2Mo_{14}O_{43}$				S	L				
$(NH_4)_2Mo_{22}O_{67}$						L	T	T	
MoO_3				S	L	L	L	L	L

$NH_3\uparrow + H_2O\uparrow$ (2)

$$(NH_4)_2Mo_4O_{13} \xrightarrow{\sim 360\ ℃} MoO_3 + NH_3\uparrow + H_2O\uparrow \quad (3)$$

$$\beta\text{-}(NH_4)_2Mo_4O_{13} \xrightarrow{316\ ℃\sim 348\ ℃} MoO_3 + NH_3\uparrow + H_2O\uparrow \quad (4)$$

$(NH_4)_4Mo_8O_{26}\cdot 2H_2O$ dehydrates prior to the thermal decomposition as follows:

$$(NH_4)_4Mo_8O_{26}\cdot 2H_2O \xrightarrow{\sim 287\ ℃} (NH_4)_4Mo_8O_{26} + H_2O\uparrow \quad (5)$$

$$(NH_4)_4Mo_8O_{26} \xrightarrow{\sim 370\ ℃} MoO_3 + NH_3\uparrow + H_2O\uparrow \quad (6)$$

Andras Kiss *et al*[4] found two other intermediate phases, namely $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$ when studying the thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

Table 1~3 show that $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$ were also identified in our experiments, which indicates obviously that the following intermediate reactions existed during the decomposition of $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ into MoO_3:

$$(NH_4)_2Mo_4O_{13} \text{ or } \beta\text{-}(NH_4)_2Mo_4O_{13} \longrightarrow (NH_4)_2Mo_{14}O_{43} + NH_3\uparrow + H_2O\uparrow \quad (7)$$

$$(NH_4)_2Mo_{14}O_{43} \longrightarrow (NH_4)_2Mo_{22}O_{67} + NH_3\uparrow + H_2O\uparrow \quad (8)$$

$$(NH_4)_2Mo_{22}O_{67} \longrightarrow MoO_3 + NH_3\uparrow + H_2O\uparrow \quad (9)$$

The DTA/TGA curves of AM-1 show that AM-1 decomposed by stages. There were three endothermic peaks in the DTA curve at about

110 ℃, 220 ℃ and 290 ℃ respectively corresponding to the three stages of weight loss in the TGA curve. From the phase composition in Table 1, it can be inferred that the thermal decomposition reactions of AM-1 at the three temperatures are:

① 110 ℃: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ decomposes into $(NH_4)_4Mo_5O_{17}$ according to equation (1);

② 220 ℃: $(NH_4)_4Mo_5O_{17}$, both in the mixture and formed by equation (1) decomposes into $(NH_4)_2Mo_4O_{13}$ according to equation (2);

③ 290 ℃: $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ in the mixture and $(NH_4)_2Mo_4O_{13}$ formed by equation (2) decompose into MoO_3 according to equations (7), (8) and (9).

As the amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in the mixture was small, the weight loss due to its decomposition at 110 ℃ was small as shown in Fig. 1(a). The amount of $(NH_4)_4Mo_5O_{17}$ which decomposed at 220 ℃ was larger, therefore the weight loss at this moment was also larger. The amount of $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ which decomposed at 290 ℃ was the largest, the weight loss at this temperature was, accordingly, the largest.

The phase composition of AM-2 and AM-3 was the same except for more $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$ in AM-3[1]. Their DTA/TGA curves were similar except that a small endothermic peak and a small weight loss existed at about 220 ℃ in the DTA/TGA curves of AM-3 in Fig. 1 (c). It is well known that $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$ is essentially identical with $(NH_4)_4Mo_8O_{26}\cdot 4H_2O$ where the water of crystallization tenaciously held through the hydrogen bond will dehydrate at a relatively higher temperature than the usual dehydration temperature around 100 ℃[2]. Accordingly, the endotherm and weight loss of AM-3 at about 220 ℃ are inferred mainly dehydration. As less $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$ existed in AM-2, there were no obvious endotherm and weight loss around 220 ℃. The phase compositions in Table 3 also indicate that the amount of $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$ in AM-3 has decreased a lot below 300 ℃ due to dehydration. From Table 2 and Table 3, it can be seen that $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ in AM-2 and AM-3 also decomposed into MoO_3 according to equations (7), (8) and (9) with $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$ as the intermediate products.

3 CONCLUSIONS

(1) When heated, AM-1 will decompose in the following steps:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \xrightarrow{\sim 110\ ℃} (NH_4)_4Mo_5O_{17} \xrightarrow{\sim 220\ ℃} (NH_4)_2Mo_4O_{13}$$

$$(NH_4)_2Mo_4O_{13} \text{ or } \beta\text{-}(NH_4)_2Mo_4O_{13} \xrightarrow{\sim 290\ ℃} (NH_4)_2Mo_{14}O_{43} \xrightarrow{\sim 290\ ℃} (NH_4)_2Mo_{22}O_{67} \xrightarrow{\sim 290\ ℃} MoO_3$$

(2) The thermal decomposition of AM-2 and AM-3 proceeds in steps of:

$$(NH_4)_2Mo_4O_{13} \text{ and } \beta\text{-}(NH_4)_2Mo_4O_{13} \text{ and } (NH_4)_2Mo_4O_{13}\cdot 2H_2O \xrightarrow{\sim 290\ ℃} (NH_4)_2Mo_{14}O_{43} \xrightarrow{\sim 290\ ℃} (NH_4)_2Mo_{22}O_{67} \xrightarrow{\sim 290\ ℃} MoO_3$$

The larger amount of $(NH_4)_2Mo_4O_{13}\cdot 2H_2O$ in AM-3 will dehydrate at about 220 ℃ prior to the decomposition.

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