POLYMORPH CONTROL OF ANTIMONY WHITE(Sb_2O_3) PREPARED BY HYDROMETALLURGY METHOD [①]

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ABSTRACT   The effects of reaction solvent, the properties of $Sb_4O_5Cl_2$ material and the ligand additives on the reaction rate and polymorph of antimony white(Sb_2O_3) in the reaction of $Sb_4O_5Cl_2$ transforming into Sb_2O_3 have been investigated by XRD and IR method. It is revealed that the reaction solvent and the properties of $Sb_4O_5Cl_2$ are the key factors affecting the reaction rate. The polymorph of antimony trioxides is determined by the reaction mechanism, *i. e.* the coordination state of the antimony activated complex. Adding a little ligand such as EDTA is the most economical and effective method of synthesizing cubic antimony white (Sb_2O_3) in hydrometallurgical transformation process.

Key words   antimony white   polymorph   antimony activated complex   structure selecting catalyst

1   INTRODUCTION

Antimony white, *i. e.* antimony trioxide, mainly has two crystal forms: cubic and orthorhombic. The cubic antimony trioxide is stable at low temperature, and changes into orthorhombic when heated to 550~ 570 ℃[1].

There are two ways for antimony white preparation, *i. e.* pyro- and hydrometallurgical methods. In pyrometallurgical process, the crystal form of antimony white can be adjusted by controlling the process conditions. However, in hydrometallurgical process, hydrolysis and neutralization of antimony trichloride usually yields orthorhombic antimony white, which can almost all change into cubic forms by vacuum-drying treatment at 260 ℃ according to Duan Xue cheng's research[2]. A series of study has proved that the pure cubic antimony trioxide can be acquired directly by adding a little EDTA or tartaric acid to the reaction system of antimony oxychloride transforming to antimony white[3]. In

this paper the authors try to systematically analyze the affecting factors and controlling method of the crystal structures of antimony white in hydrometallurgical process, providing a theoretical guidance for preparing pure cubic antimony white by hydrometallurgical method.

2   EXPERIMENTAL

2.1   Experimental materials

Methanol(CH_3OH), ether($C_2H_5OC_2H_5$), ammonium tartrate($(NH_4)_2C_4H_4O_6$), antimony trichloride($SbCl_3$) are all analytically pure, the high concentration ammonia water is chemically pure, and the water is distilled water.

The antimony oxychloride is prepared by hydrolyzing the 6 mol/ L antimony trichloride solution, and except particular notice it is filterd, and dried at 80~ 90 ℃ for 3~ 5 h. Its composite is $Sb_4O_5Cl_2$ by XRD analysis.

2.2   Experimental conditions

The transforming reaction was undertook in

a thermostatical magnetic agitator, the reaction temperature was 25~ 30 ℃, mass of $Sb_4O_5Cl_2$ was 3. 2g, and the other experimental conditions were listed in Table 1. When the reaction finished, the suspension was filtered at once, and the solid products were dried for 3~ 5h at 80 ℃.

2. 3 Analysis and examination

The composites and crystal structures of the reaction powder products were determined by XRD and IR analysis.

3 RESULTS

3. 1 Experimental results

Fig. 1 and Fig. 2 are the XRD patterns and IR patterns of the reaction products respectively. For the determination of the composites and the compound structures mark in the patterns, according to JCPDS the $d(d)$ and relative intensity of the composition in XRD figure for $Sb_4O_5Cl_2$ monoclinite are 6. 19(50), 3. 703(35), 3. 286 (100), 3. 120(85), 2. 05(30), for cubic Sb_2O_3 are 3. 219(100), 2. 788(35),   1. 974(33),

1. 6812(31), 6. 439(17), and for orth. Sb_2O_3 are 3. 142(100),   3. 118(75),   3. 492(25), 3. 74(20), 1. 8046(20). In IR pattern figure, the featured absorption peak of cubic Sb_2O_3 is $740\,cm^{-1}$[4], which is consistent with all references. However, about the differences in the featured absorption peaks of orth. Sb_2O_3, literature[4] says $690\,cm^{-1}$, and literature [5] says 740, 540, $455\,cm^{-1}$. Minoru Hasegawa analyzed the compositions of the reaction products according to the latter standard[5], but in fact, the reaction product which has absorption peaks at 745, 689, 589, $458\,cm^{-1}$ is the mixture of the cubic and orth. Sb_2O_3, Therefore, the featured absorption peak of orth. Sb_2O_3 is $690\,cm^{-1}$ and it is agreeable with our experimental results. In addition, $Sb_4O_5Cl_2$ has featured absorption peak at $839\,cm^{-1}$. According to the standard, the composites and compound structures of the products can be determined and the results are listed in Table 1.

In Table 1, it is demonstrated that there are some differences in the XRD and IR analy-

Table 1 The conditions of experiment and the compositions of products

No.	Reaction system	Time / min	Product composition XRD	Product composition IR	Note
1	$NH_3 \cdot H_2O(40\,cm^3,\ 1\%)$	10	$Sb_2O_3(O)$ [a]	$Sb_2O_5Cl_2$ $Sb_2O_3(O)$	
2	$NH_3 \cdot H_2O(40\,cm^3,\ 1\%) + (NH_4)_2L$[d]$(2.5\,cm^3)$	10	$Sb_2O_3(C)$ [b]	$Sb_2O_5Cl_2$ $Sb_2O_3(C)$	
3	$CH_3OH(40\,cm^3) + NH_3 \cdot H_2O(10\,cm^3, 5\%)$	60	$Sb_4O_5Cl_2$		
4	$C_2H_5OC_2H_5(40\,cm^3)$	30	$Sb_4O_5Cl_2$		
5	$C_2H_5OC_2H_5(40\,cm^3) + NH_3 \cdot H_2O(10\,cm^3, 5\%)$	60	$Sb_4O_5Cl_2(48.6)$ [c] $Sb_2O_3(O\ 51.4)$	$Sb_4O_5Cl_2$ $Sb_2O_3(O)$	
6	$C_2H_5OC_2H_5(40\,cm^3) + NH_3 \cdot H_2O(10\,cm^3,\ 5\%)$	30	$Sb_2O_3(O\ 93.1)$ $Sb_2O_3(C\ 6.9)$	$Sb_2O_3(O)$	$Sb_4O_5Cl_2$ not filtered and dried
7	$C_2H_5OC_2H_5(38\,cm^3) + NH_3 \cdot H_2O(10\,cm^3, 5\%) +$ $(NH_4)_2L(2.5\,cm^3)$	30	$Sb_4O_5Cl_2(82.6)$ $Sb_2O_3(O\ 17.4)$		
8	$C_2H_5OC_2H_5(38\,cm^3) + NH_3 \cdot H_2O(10\,cm^3, 5\%) +$ $(NH_4)_2L(2.5\,cm^3)$	60	$Sb_4O_5Cl_2(68.0)$ $Sb_2O_3(C\ 32.0)$	$Sb_4O_4Cl_2$ $Sb_2O_3(C)$	
9	$NH_3 \cdot H_2O(100\,cm^3, 1\%) + SbCl_3(2\,mol/L, 5\,cm^3)$	10	$Sb_2O_3(C\ 81.0)$ $Sb_2O_3(O\ 19.0)$		add $SbCl_3$ solution directly into ammonia water

Notes: a) $Sb_2O_3(O)$ —Orthorhomic Sb_2O_3; b) $Sb_2O_3(C)$ —Cubic Sb_2O_3;
         c)   the number is the semi-quantitative analysis result of the composition of the products by XRD;
         d) $(NH_4)_2L$ —$(NH_4)_2H_4C_4O_6$, $C=1\,mol/L$.
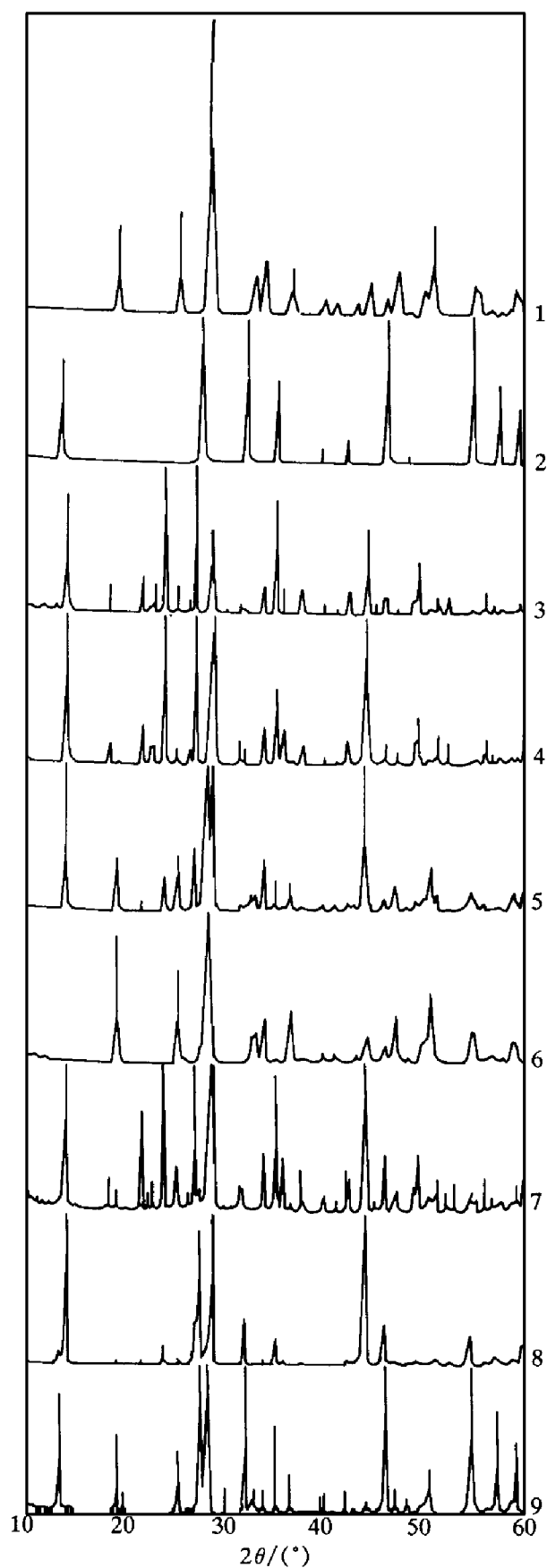
Fig. 1   XRD patterns of products

Fig. 2   IR patterns of some products

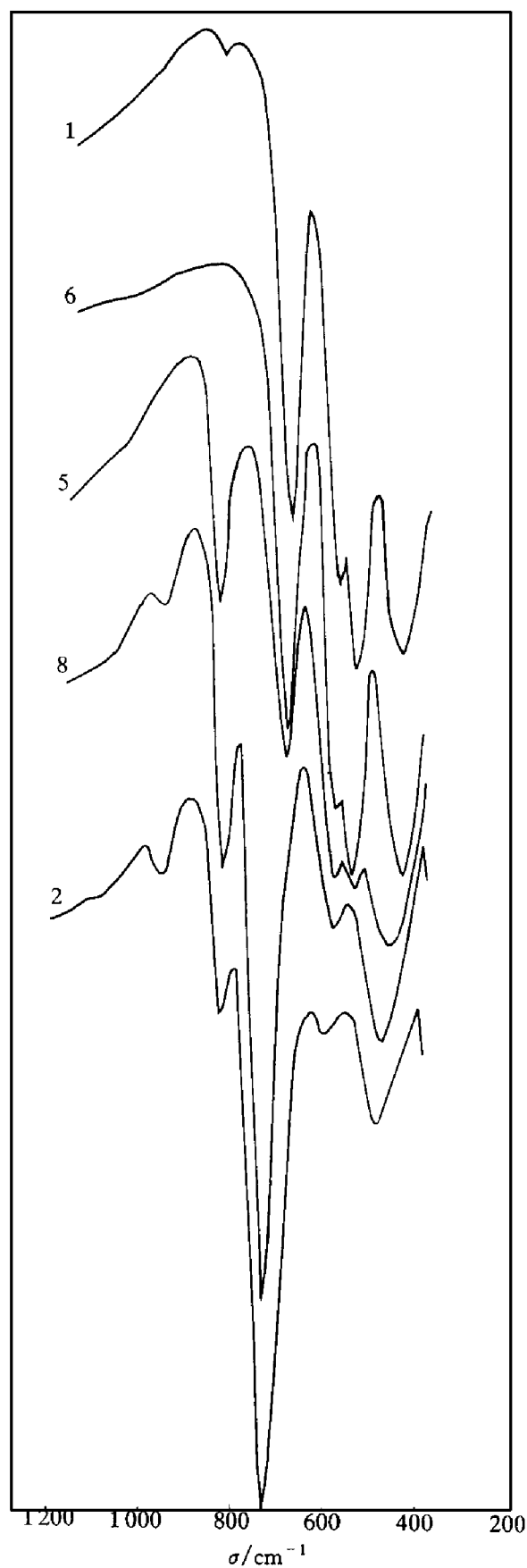ses: (1) the samples of No. 1 and No. 2 have a small absorption peak at 839 cm^{-1} in IR pat-

terns, which shows a little $Sb_4O_5Cl_2$ exists in the sample, but there is no $Sb_4O_5Cl_2$ according to

XRD patterns. (2) acording to XRD analysis, there is 6. 9% cubic Sb_2O_3 in sample No. 6, but it is not shown in IR patterns in reverse. These differences can be regarded to be caused by the differences of the sensitivities of two methods.

3. 2　Analysis of the factors affecting the reaction rate

Table 1 reveals that the reaction rate of $Sb_4O_5Cl_2$ turning into Sb_2O_3 varies very much in different solvent systems, and it increases according to the order of $CH_3OH < C_2H_5OC_2H_5 < NH_3 \cdot H_2O$. This can be explained by the differences of their alkalinity. $Sb_4O_5Cl_2$ is a Lewis acid, Sb_2O_3 is a amphoteric oxide, in the reaction process of $Sb_4O_5Cl_2$ transforming to Sb_2O_3. The stronger the alkalinity of reaction solvent, the faster the reaction rate is. The alkalinity rises in the order of $CH_3OH < C_2H_5OC_2H_5 < NH_3 \cdot H_2O$, so the reaction rate increases in the same order. In fact, it has also been proved in Hasegawa's study[6].

In addition, the properties of $Sb_4O_5Cl_2$ materials play an important role in the reaction rate. In the same system, the reaction rate when the $Sb_4O_5Cl_2$ isn't filtered and dried is almost 1 time faster than that when the $Sb_4O_5Cl_2$ is filtered and dried. This is because that two kinds of $Sb_4O_5Cl_2$ materials differ very much in their reaction activities caused by the structure defects and absorption water.

4　THE POLYMORPH OF ANTIMONY WHITE CONTROL

4. 1　The effect of reaction solvent

In early 1970's, it was accidentally found by Abrland that the cubic Sb_2O_3 could be prepared by washing the metastable phase Sbop(55) produced by hydrolysis of antimony chlorate solution with methanol for a long time at room temperature[7]. moreover, while studying the hydrolysis of $Sb (OSiR_3)_3$ compounds, the effects of the reaction solvent on the polymorph of antimony trioxide were found by Hasegawa et al, that the cubic Sb_2O_3 can be obtained by hydrolysis of the $Sb(OSiR_3)_3$ compounds in $H_2O/$

CH_3OH solvent system, but in CH_3COCH_3/ H_2O system, as the R group enlarges, the polymorph of Sb_2O_3 obtained goes through the transformation course from cubic via the mixture of cubic and orth. to pure orth. . So the authors think that it is caused by the different reaction mechanism in two solvent systems[6].

In organ metallic chemistry reaction, solvent affects the electronic structures and geometries of the complexes in solution and then determines the manner of bond breaking and organic groups redistributing[8]. So does in the system of preparing antimony trioxide by hydrolyzing of $Sb (OSiR_3)_3$. The CH_3OH molecule is small with little steric hindrance and active hydrogen, so Sb(III) can easily react with it to form six-coordination complexes with octahedral structure. Thus, cubic Sb_2O_3 is attained by hydrolysis of $Sb(OSiR_3)_3$ in CH_3OH/ H_2O system. However, CH_3COCH_3 is bigger than CH_3OH in steric hindrance, the steric hindrance increases great enough to hinder the Sb(III) to form the six coordination complexes, and it can only form the three coordination complexes instead.
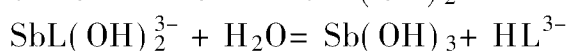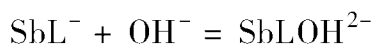
From the above analysis, it is concluded that, cubic Sb_2O_3 can be obtained when antimony activated complex is six coordination with octahedron structure, and only orth. Sb_2O_3 is obtained when the antimony activated complex is three coordination with tetrahedra structure. In fact, it is also proved by this experiment that if 2 mol/ L $SbCl_3$ solution is added to ammonia water, the content of cubic Sb_2O_3 in the reaction products of antimony trioxide is about equal to the content of $SbCl_6^{3-}$ in $SbCl_3$ solution.

4. 2　The action mechanism of polymorph modifying additives

Antimony oxychloride is monoclinic space group, the antimony bonds are intermediate between covalent and ionic binding, the Sb and O atoms form the Sb —O —Sb infinite chains just as the same as that of orth. Sb_2O_3[9]. So if the coordination condition isn't changed in the trans formating reaction course, the $Sb_4O_5Cl_2$ will change into orth. Sb_2O_3, moreover, because of the electronic repellence of O and Cl atoms bind-
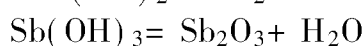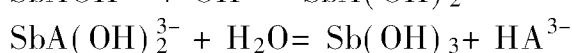
ing with Sb(III), and the effects of the lone pair of Sb(III) itself, it is very difficult for Sb(III) in $Sb_4O_5Cl_2$ to accept the electrons from the solvent donor, therefore, even in the system of $CH_3OH/NH_3 \cdot H_2O$, it can't change its coordination condition to cubic Sb_2O_3. Only the electron donor ligand with strong coordination ability, such as EDTA or tartrate ions, can make Sb(III) in $Sb_4O_5Cl_2$ change the coordination condition, and produce the cubic Sb_2O_3. In solution, Sb(III) reacts with EDTA or tartrate ions, forms $Sb(EDTA)^-$ or $Sb_2(H_2C_4O_6)_2^{2-}$.

The coordination number of Sb(III) in $Sb(EDTA)^-$ is already six. In the hydrolysis course, OH^- ion replaces the coordination atoms binding with Sb(III) step by step, and the final hydrolysis product is cubic Sb_2O_3. The full reaction course is listed as following[10].

$$SbL^- + OH^- = SbLOH^{2-}$$
$$SbLOH^{2-} + OH^- = SbL(OH)_2^{3-}$$
$$SbL(OH)_2^{3-} + H_2O = Sb(OH)_3 + HL^{3-}$$
$$2Sb(OH)_3 = Sb_2O_3 + 3H_2O$$

where　L represents $EDTA^{4-}$ ion.

$Sb_2(H_2C_4O_6)_2^{2-}$ is a binuclear complex ion, the coordination number of Sb(III) is four. It first adds OH^- to form 5- and 6- coordination complex, then hydrolyzes to yield the cubic Sb_2O_3 with the pH in solution rising[11].

$$Sb_2A_2^{2-} + 2OH^- = 2SbAOH^{2-}$$
$$SbAOH^{2-} + OH^- = SbA(OH)_2^{3-}$$
$$SbA(OH)_2^{3-} + H_2O = Sb(OH)_3 + HA^{3-}$$
$$Sb(OH)_3 = Sb_2O_3 + H_2O$$

where　A denotes tartrate ion.

From the above reaction course, it is found that the effect of $EDTA^{4-}$ and tartrate ion is to alter the coordination condition of Sb(III), so the chemical reaction course is controlled to produce cubic Sb_2O_3. They are essentially the structure selecting catalysts of the reaction of $Sb_4O_5Cl_2$ transforming to Sb_2O_3. They themselves aren't consumed in the reaction process, and their effective dosages are determined by the solubility and stability of complexes with Sb(III) and their chemical reaction rate, e. g. for $EDTA^{4-}$, only 1% (in mole) $Sb_4O_5Cl_2$ is enough.

5　CONCLUSIONS

(1) The reaction rate of $Sb_4O_5Cl_2$ transforming to Sb_2O_3 has a close relation with the reaction solvent and the properties of $Sb_4O_5Cl_2$ materials, the more basic the solvent, the faster the reaction.

(2) The polymorph is mainly determined by the reaction mechanism, i. e, the coordination state of the activated complex. While the coordination number of Sb(III) in activated complex is 6, cubic Sb_2O_3 is obtained; while it is 3, orth. Sb_2O_3 is obtained.

(3) $EDTA^{4-}$ and tartrate ions are the structure selecting catalysts to the reaction of $Sb_4O_5Cl_2$ changing to cubic Sb_2O_3, they have strong coordination action with Sb(III) to make Sb(III) change the steric coordination number from 3 to 6 coordination.

REFERENCES

1　Zhao Tiancong. The Metallurgy of Antimony. Changsha: Central South University of Technology Press, 1988: 16– 20.
2　Duan Xuecheng, Zhao Tiancong. Chinese Journal of Nonferrous Metals, (in Chinese), 1996, 6(1): 36.
3　Zhong Hui. Mast. thesis, (in Chinese). Central South University of Technology, 1991: 40.
4　William B White, Rustum Roy. The American Mineralogist, 1964, 49: 1670.
5　Cody C A, Dicarlo L, Darlington R K. Inorg Chem, 1979, 18: 1572.
6　Minoru Hasegawa, Hideyuki Matsumoto. Nippon Kagaku Kaishi, (in Japanese), 1995, (7): 550.
7　Abrland S, Bouin Janolov. Acta Chemica Scandinavica, 1974, A28: 1089.
8　Petrosyan V S, Yashina NS, Reutov O A et al. Journal of Organometallic Chemistry, 1973, 52: 321.
9　Edstrand Maga. Acta Chemica Scandinavica, 1947, 1: 178.
10　Ozer U Y, Bogucki R F. Journal Inorg Nucl Chem, 1971, 33: 4143.
11　Anderegg G, Malik S. Helvetica Chimica Acta, (in Germany), 1970, 53(3): 577.

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