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Oxidation roasting of molybdenite concentrate

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Abstract: In order to investigate the oxidation roasting of molybdenite concentrate in pure oxygen atmosphere, experiments at 673, 723, 773, 873 and 973 K were carried out. The phase transitions and morphology evolutions of the samples obtained at different temperatures after reacting for different time were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that molybdenite concentrate was oxidized directly to MoO₃ in pure oxygen atmosphere. There were remarkable changes of the morphologies of products with the increase of the roasting temperature. It was also found that sintering phenomenon occurred during the roasting process in pure oxygen when the temperature was above 873 K. The composition of sintered sample was mainly comprised of MoO₃ and some unreacted MoS₂.

Key words: oxidation roasting; molybdenite concentrate; morphology; sintering

1 Introduction

Molybdenite concentrate has excellent properties in catalysis and lubrication [1,2]. Also, molybdenite concentrate (about 90% MoS₂) is the essential ore mineral of the molybdenum industry for the production of technical grade molybdenum trioxide, which is further used to produce molybdenum dioxide [3], molybdenum, ferromolybdenum alloy and other pure molybdenum compounds, such as ammonium paramolybdate, sodium and calcium molybdate. The oxidation roasting of molybdenut trioxide. At present, the oxidation roasting of molybdenite concentrate has been commercially carried out in multiple heart furnace and fluidized bed furnace. The main reaction during the oxidation process is

$$MoS_2 + 3.5O_2 = MoO_3 + 2SO_2$$
 (1)

The change of the standard free energy of Reaction (1) is given by the following equation [4]:

$$\Delta G/(\text{J} \cdot \text{mol}^{-1}) = -1074744.08 + 61.38T \text{lg}T - 2.26 \times 10^{-2} T^2 + 2.60 \times 10^{-6} T^3 + 57.74T$$
(2)

The equilibrium constant K of Reaction (1) at temperature T can be calculated by the following equation:

$$\lg K_T = -\frac{\Delta G}{2.303RT} \tag{3}$$

Owing to the large equilibrium constant of the above reaction, for instant, up to 10^{52} when the temperature is 873 K, the oxidation reaction of molybdenite concentrate in air or pure oxygen could be considered to be an irreversible one.

Many investigations have been done to study the oxidation roasting of molybdenite concentrate. ŽIVKOVIĆ and ŠESTÁK [5] studied the roasting process of MoS₂ synthesized in the laboratory and determined the kinetic parameters using the Kissinger and the Ozawa methods. SHIGEGAKI et al [6] investigated the oxidation mechanism of pure MoS₂ using the TG-DTA method, and reported that oxidation process of MoS₂ powder is controlled by a threedimensional boundary reaction. MARIN et al [7] carried out oxidation roasting using a thin layer of sample in a muffle furnace in air in order to simulate the reactions taking place in the multiple heart furnace. The results showed that the rate of oxidation was very slow below 713 K, and then it increased and remained constant from about 813 K to 913 K. A kinetic model involving the intermediate phase of MoO₂ was proposed (MoS₂ \rightarrow $MoO_2 \rightarrow MoO_3$). UTIGARD [8] conducted a large number of experiments about the oxidation roasting of molybdenite concentrate using a thermal gravimetric

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unit on a small scale both in air and oxygen atmosphere. The solid-state reaction between MoS_2 and MoO_3 to form MoO_2 was found to take place. WILKOMIRAKY et al [9] studied the reaction of molybdenite concentrate with oxygen and air in a hot-stage microscope and reported that acicular crystals of MoO_3 grown rapidly outward from the molybdenite. KIM et al [10] reported that the rate of mass loss decreases as the particle size increases when roasting the low grade Mongolian molybdenite concentrate in dried air. However, the particle size effect was slight when the molybdenite particle size was less than 67 μ m. Very recently, a looping oxidation process with the aim to decrease energy consumption has been proposed by MCHUGH et al [11].

Although many investigations on the oxidation roasting of molybdenite concentrate have been done, most of them were preceded in air atmosphere. Nowadays, oxygen-enriched air technology has been widely used to the iron-making process in blast furnace and it greatly improves the smelting efficiency. Similarly, the present study aims to investigate the oxidation roasting of molybdenite concentrate in pure oxygen in order to explore a new way of treating molybdenite. The phase transitions and morphology evolutions during the oxidation process will be analyzed.

2 Experimental

2.1 Sample preparation

The molybdenite concentrate from Jinduicheng Molybdenum Industry Co., Ltd., Xi'an, China, was used as the raw material. The mass fraction of Mo content is about 54.89%. The main impurities in the molybdenite concentrate are sulfides or oxides of lead, copper, calcium, iron and silicon, etc. The chemical composition of the studied molybdenite concentrate is given in Table 1.

 Table 1 Chemical composition of molybdenite concentrate (mass fraction, %)

(muss muchon, vo)							
	Мо	S	Pb	b Si		Cu	Ca
	54.89	33.27	0.0	8	1.83	0.07	0.28
-	Fe	Al	Κ	Ti	С	Р	Total
	1.12	0.19	0.14	0.04	0.17	0.01	92.09

The X-ray diffraction (XRD) pattern of molybdenite concentrate sample is shown in Fig. 1. The main peaks are well-defined to be MoS_2 . From Fig. 2, it can be seen that molybdenite concentrate particle has a layer structure and a wide particle size distribution ranged from several microns to 100 µm.



Fig. 1 XRD pattern of studied molybdenite concentrate



Fig. 2 SEM images of molybdenite concentrate sample: (a) Polished; (b) Unpolished

2.2 Apparatus and procedure

Figure 3 shows the schematic diagram of the apparatus. Alumina crucibles with 50 mm in length, 25 mm in width and 20 mm in height were used. At first, molybdenite concentrate was dried at 383 K in the oven for 12 h. In each experimental run, a sample of about 3 g (about 5 mm in thickness) was used and filled into the alumina crucible. After the crucible with the sample was placed into the quartz tube, argon was purged to remove air from the quartz tube. Then the quartz tube was put



Fig. 3 Schematic diagram of experimental apparatus: 1—Flow meter; 2—Inner quartz tube; 3—External quartz tube; 4—Samples; 5—Si-C electric furnace; 6—Thermocouple; 7—Empty beaker flask; 8—Beaker flask with water

into the electrical furnace with the heating element of Si–C rods, the temperature of which was already raised to the desired value. When the temperature was stabilized, the argon was switched to pure oxygen to start the oxidation reaction. After reacting for a certain time, gas inlet was switched to argon again, and the quartz tube was taken out quickly to cool the sample to the room temperature. The mass loss after the oxidation process was measured. In the present study, oxidation experiments at five temperatures (673, 723, 773, 873 and 973 K) for different reacted time were conducted.

In all the experimental runs, a constant oxygen flow rate of 400 mL/min was kept during the oxidation process. XRD (Model, TTR III, Japan) and SEM (Model S250MK3, CAMBRIDGE) were used to analyze the samples.

3 Results

3.1 Mass loss

The mass loss (η) was calculated with the following equation:

$$\eta = \frac{m_0 - m_t}{m_0} \times 100\%$$
 (4)

where m_0 and m_t are the masses of the initial sample and that reacted for a period time of *t*, respectively. The experimental data are shown in Fig. 4. It is clearly seen that the rate of reaction is very slow at 673 K. Even the roasting time was up to 100 min, there was a very small mass loss. Meanwhile, the maximum mass loss is different at different roasting temperatures and the value increases with the increase of temperature. The plateaus were reached after reacting for 20 min in all cases except the case when the temperature was 673 K. One surprising aspect of the roasting tests was that the sample was partially sintered and appeared to stick to the bottom of alumina crucible when reacting at 873 K for 20 min or



Fig. 4 Mass loss versus reaction time curves for molybdenite concentrate

longer. At 973 K, the sintering phenomenon occurred when reacting for 15 min. However, when the temperature was lower than 873 K, there was no sintering occurred even roasting for 1 h. It was also found that the color of the product continuously changed as the reaction proceeded. For example, when samples were roasted at 873 K, the color changed from black or grey to white with a light-greenish tint, as shown in Fig. 5. Furthermore, on the surface of product, many acicular, elongated and thin products were produced.

3.2 XRD analysis

The X-ray diffraction patterns of products roasted at 723, 773 and 873 K are shown in Figs. 6(a)-(c), respectively. Figure 6(a) shows that after 15 min, there are some peaks for MoO₃, but the main phase is still MoS₂ in the molybdenite concentrate. The X-ray diffraction pattern for sample reacted for 20 min is very similar as that reacted for 15 min. Even if the reacting time is as long as 60 min when mass loss is almost stopped as shown in Fig. 4, there are still many unreacted MoS₂. Therefore, the completed oxidation of MoS₂ is very hard at 723 K. The X-ray diffraction patterns for



Fig. 5 Color change after blending associated with oxidation in pure oxygen at 873 K

sample reacting at 773 K as shown in Fig. 6(b) are somewhat similar to those of Fig. 6(a). The obvious difference is that when the roasting time is longer than 20 min, most of the MoS₂ could be oxidized to MoO₃. However, when the temperature is up to 873 K, as shown in Fig. 6(c), no peaks of MoS₂ are detected in the final products, and the main constituent is MoO₃ after reaction for 20 min.

3.3 Microscopic examination

Scanning electron micrographs of molybdenite concentrate sample oxidized in pure oxygen at 873 K for various time are shown in Fig. 7. After reacting for 5 min, as shown in Fig. 7(a), the morphology of product is similar to the raw molybdenite concentrate (Fig. 2 (b)). Figures 7(b) and (c) show that the morphologies have significant changes after reaction for a long time when compared with Fig. 7(a). It can be found that as the reaction proceeds, large MoS₂ particles disappeared with the formation of a large amount of plate-shaped MoO₃. When sampling the surface product for observation, as shown in Fig. 7(d), almost all the MoO₃ were plate-shaped and acicular or elongated.

Comparisons of morphologies of the samples oxidized in pure oxygen at different temperatures for various time are shown in Fig. 8. At 723 K, as shown in Fig. 8(a), the compact MoO_3 is evident. Whereas, at 773 K, as shown in Fig. 8(b), the platelet-shaped crystals can be seen and some small crystals appear to be broken from the oxidized particles and a lot of fragmentations can be seen easily, which may be the result of the release of gaseous SO₂. The particles have a tendency to



Fig. 6 XRD patterns of products after oxidation roasting of molybdenite concentrate at different temperatures for various time: (a) 723 K; (b) 773 K; (c) 873 K

agglomerate together. At 873 K, as shown in Fig. 8(c), the transformation to MoO_3 is completed with crystals growing away from the original MoS_2 . Since these crystals grow out away from the surface, it appears that a vapor phase mechanism is involved, i.e., gaseous MoO_3 forms at the nucleation site and then condenses as it leaves the hot reaction region.



Fig. 7 SEM images of molybdenite concentrate samples oxidized in pure oxygen at 873 K for various time: (a) 5 min; (b) 10 min; (c) 20 min; (d) Surface acicular products oxidized for 120 min



Fig. 8 SEM images of molybdenite concentrate samples oxidized in pure oxygen at different temperatures: (a) 723 K for 60 min; (b) 773 K for 60 min; (c) 873 K for 10 min

4 Discussion

4.1 Formation mechanism of sintering

Previously, many researchers [7,8] have found that there were sintering or agglomerating phenomena at the temperatures above 873 K in air when oxidizing molybdenite concentrate. In the present study, the sintering took place from 20 min at 873 K, when MoS_2 disappeared as shown in Fig. 6(c), and from 15 min at 973 K, while at other temperatures, there was no sintering occurred.

Figure 9 shows the XRD pattern for sintering at 873 K for 120 min. It is obviously seen that its main component was MoO₃, but it also had some unreacted MoS_2 . This means that the molybdenite concentrate had not been oxidized completely at the bottom due to the sintering. Obviously, when the temperature was increased up to 973 K, the sintering phenomenon is more serious, which may be resulted from the high local reaction rate which released lots of heat leading to a much higher local temperature. Since the melting point of MoO_3 is 1068 K [12,13], when the local temperature is higher than it, the liquid phase will present which results in the occurrence of sintering. However, since the vapor pressure of MoO₃ increases with the increasing temperature [14,15], the sublimation becomes more significant at 973 K than that at 873 K, thus the mass loss is larger than that at 873 K, as shown in Fig. 4.



Fig. 9 XRD pattern for sintered sample oxidized at 873 K, 400 mL/min O₂ for 120 min

The morphologies of the sintered products are shown in Fig. 10. It is observed that smooth surface was produced due to the fusion of particles which change the surface morphology greatly. EDS analysis for the smooth surface shows that the main component is MoO₃, but with low content of other metal oxides, such as calcium oxide. Therefore, the glazing of molybdenite concentrate may be caused by the formation of low melting of eutectic metal oxides and molybdenum trioxide.



Fig. 10 SEM images of sintered sample: (a) 873 K for 40 min; (b) 973 K for 15 min; (c) 973 K for 20 min

4.2 Oxidation mechanism

WILKOMIRSKY et al [9] carried out the oxidation of molybdenite concentrate in a hot-stage microscope and visually observed the rapid growth of MoO₃ crystals outward other than inward. The growth of these crystals was interpreted as a vaporization–condensation mechanism, in which the product MoO₃ is heated to a relatively high temperature by the exothermic reaction, and then it vaporizes from the surface, at last condenses on the protruding oxide crystals.

As seen from Fig. 8, as the temperature increases from 723 K to 873 K, molybdenum oxide crystallizes to polyhedral and plate-shaped particles that grow directionally. This phenomenon changes the shape of the particles dramatically. Directional crystallization of MoO_3 could remove oxide layer from the surface of MoS_2 particles, which is in agreement with the work of WILKOMIRSKY et al [9].

4.3 Formation of MoO₂

In the present study, MoS_2 powder was oxidized to MoO_3 in a single step in pure oxygen without any intermediate oxide. These results are in agreement with those of WILKOMIRSK et al [9,16], DOHEIM et al [17], ROSS and SUSSMAN [18] and SHIGEGAKI et al [6], but differ from the results of MARIN et al [7], UTIGARD [8], ONG [19], ZELIKMAN and BELYAEVSKAYA [20], and COUDURIER et al [21] in which MoO_2 as an intermediate oxidative product was produced before the formation of MoO_3 .

In order to explain the discrepancies between the results, additional experiments in air atmosphere were carried out. Figure 11 shows the differences of the products produced under pure oxygen and air atmosphere under identical conditions. It is clearly seen that the rate of oxidation in oxygen is much larger than that in air, and it took 60 min to reach plateau in air, while in pure oxygen, it only needed 20 min. Figure 12 shows the SEM images of products after roasting molybdenite concentrate in air and oxygen. It is clearly seen that the micrographs of products are similar to each other (the black part is SiO₂). In addition, when compared with the raw material (Fig. 2), it can be seen that there are no obvious changes on morphologies of the cross sections of different samples and it is hard to identify MoO₂, MoO₃ and MoS₂. Figure 13 shows the XRD patterns of products after roasting molybdenite concentrate in air for different time. Unexpectedly, it can be seen that MoO₂ could be formed when roasting in air. Thus, the high oxygen potential in pure oxygen atmosphere may be the reason for the disappearance of intermediate phase MoO₂.



Fig. 11 Mass loss versus time for molybdenite concentrate at 873 K in oxygen and air



Fig. 12 SEM images of products obtained at 873 K for various time: (a) 10 min in pure oxygen; (b) 20 min in air



Fig. 13 XRD patterns of products after oxidation roasting of molybdenite concentrate at 873 K in air: (a) For different time; (b) Amplified XRD pattern

5 Conclusions

1) The roasted sample begins to sinter at 873 K in pure oxygen. The compositions of the sintered products include MoO_3 and unreacted MoS_2 .

2) The reaction rate is very slow when roasting at 673 K and the sublimation of MoO_3 is significant at 973 K.

3) The intermediate oxide, MoO₂, could be detected when roasting molybdenite concentrates in air atmosphere.

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辉钼精矿的氧化焙烧

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摘 要:为研究辉钼精矿的氧化焙烧机理分别在 673、723、773、873、973 K 下进行氧化焙烧实验。分别采用 X 射线衍射(XRD)和扫描电子显微镜(SEM)对氧化过程中产物的物相和形貌进行分析。结果表明,在纯氧条件下, MoS₂ 直接氧化成 MoO₃,并且随着焙烧温度的升高,产物的形貌发生了明显变化。在纯氧气氛下,当温度高于 873 K 时有烧结现象发生,烧结物大部分是由氧化产物 MoO₃组成,同时含有少量未氧化完全的 MoS₂。 关键词:氧化焙烧;辉钼精矿;形貌;烧结