



Research of the dissolving capacity of molybdenite in the white matte



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ABSTRACT

The matte smelting method was developed to treat molybdenite using the white matte as the dissolvent. The key for achieving the process depended on whether or not molybdenite can form the molybdenum matte. The dissolving capacity of molybdenite in the white matte was evaluated in this study. The effects of the ratio of molybdenite and white matte and the melting temperature on the matte melting were investigated. In addition, given that white matte and molybdenite contained various kinds of impurities, the effects of the Fe content and the grade of matte on the solubility of molybdenite were also researched. The research results showed that with 0–20% MoS₂ addition at 1250 °C, the MoS₂ content within the matte increases with the MoS₂ addition reaching a maximum content of 14.95%. A higher level of 20% of MoS₂ addition resulted in a steep decline in the MoS₂ content. The increase of Fe contents in the white matte will cause the reduction of the solubility of MoS₂ in the matte. In addition, an excessive Cu content in the white matte reduced the dissolving capacity of molybdenite in the copper matte. As the copper content of white matte reached 20%, the dissolved Mo was only 9.33%.

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1. Introduction

Molybdenum was the important strategic metal and was applied in the field of iron, petrochemical, aerospace and national defense. Molybdenite was the major mineral of molybdenum. During the metallurgical process of molybdenite, the sulfide (MoS₂) firstly changed into oxide (MoO₃) and then separated from the accompanying impurities [1]. The treatment technology of molybdenite mainly included the pyro- and hydro-metallurgical processes [2]. The multiple hearth furnace, fluidized bed roaster, rotary kiln and reverberatory furnace were mainly adopted to roast the molybdenite in the pyrometallurgical process [3–6]. However, the roasted product, MoO₃, easily sublimed due to its low boiling point, which caused the loss of molybdenum. Therefore, the reacting rate must be controlled and heat dissipation must also be enhanced to ensure the roasting temperature not to exceed 600 °C. Furthermore, a high quality sulfuric acid is difficult to achieve since the concentration of SO₂ flue gas was generally too low (3% for fluidized bed roaster, 0.8–3% for multiple hearth furnace and 0.8–2% or even more low for rotary kiln). It's hard to prepare high quality sulfuric acid using the low SO₂ flue gas. The roasting flue gas will cause the air pollution by many factories. The production capacity for hydrometallurgical treatment process of molybdenite was too low. The lining titanium autoclave must be used during the acid or basic oxygen pressure leaching. Because these reaction processes have high requirement for the leaching equipment. In addition, if the strong oxidizer such as Cl₂,

H₂NO₃ or NaClO, were to be employed in hydrometallurgical treatment process, the treatment cost would increase and toxic gas would be produced [7–9]. Therefore, the new metallurgical method needs to be developed to treat molybdenite [10].

In our previous research, the melting salt oxidation technology of molybdenite concentrate was studied [11,12]. In this method, Na₂CO₃ or Na₂SO₄ was used as the reaction medium to dissolve the molybdenite by forming the low valence thio-molybdate. After blowing air for only 10 min, the mixture melting salt can be oxidized into Na₂MoO₄ and SO₂. But because Na₂CO₃ and Na₂SO₄ are part of the oxide melt, and the produced Na₂MoO₄ is a part of the complex oxide instead and can easily be dissolved in the melting salt, it was difficult to separate Na₂MoO₄ from the mixture. Therefore, the pure molybdenum oxide cannot be obtained directly. If a melt wherein only the molybdenite and not molybdenum oxide can be dissolved, then the molybdenum separation will be much easier to process. It was obvious that sulfide melt possessed this effect and can achieve this purpose. Indeed, it would be of great interest if the molybdenite can dissolve within the sulfide and form the sulfide melt, resembling the melting matte which is the middle product of copper or nickel smelting. The dissolving process of molybdenite was equivalent to the process of matte smelting, and the oxidative desulfurization process was actually the matte converting. The key for achieving the process depended on whether or not molybdenite can form the molybdenum matte. Kennecott [13] had researched the recycling of valuable metals from the furnace slag of copper smelting. The research results showed that copper can enter into ferric sulfide melt to form the low-copper matte under the reduction condition. It was of interest that the molybdenum of furnace slag together with copper also entered into matte. In addition, Outokumpu

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[14] had researched the behavior of impurity elements during the process of copper flash smelting. It found that even the grade of copper matte was lower molybdenum can be selectively oxidized and enriched in slag. It indicated that small amount of molybdenite accompanied in the copper concentrate was more easily oxidized compared with other sulfides. Combined with research results of two companies, it inspired us that molybdenite can react with metal sulfide to form molybdenum matte which can be separated from the melting matte by converting.

Based on above analysis, the matter smelting of molybdenite was evaluated using the white matter as dissolvent. The effects of the ratio of molybdenite and white matte and the melting temperature on the matte melting will be investigated in this research. In addition, given that white matte (Cu_2S) and molybdenite contained various kinds of impurities, the effect of the Fe content and the grade of matte on the solubility of molybdenite also will be researched.

2. Experimental

White matte, molybdenum disulfide, pyrite and copper powder were used as the raw materials. White matte was provided by Jiangxi Copper Co., and its particle size was 46 μm . Its composition and phase was showed in Table 1 and Fig. 1, respectively. Molybdenum disulfide supplied by Jinduicheng Molybdenum Group Co., Ltd. contained Mo 55.0% and S 36.7% and its particle size was 1.45 μm . Pyrite was composed of Fe 36.93% and S 42.20%. Copper powder with 74 μm was the analytically pure grade.

100 g of molybdenite, white matte and other materials according to the required composition was well mixed in the mortar. Then the mixture was put into the corundum crucible and was heated to the specified temperature. After preserving heat for 4 h, in order to keep the state of melt and reduce the composition segregation caused by slow cooling, the melt blends was cooled rapidly in the air. After cooling and grinding, the composition of melt was assayed and the phase was determined by XRD (Rigaku Corporation, Dmax/2550VB+, Japan). Mo was assayed with the ultraviolet spectrophotometer (Beijing general analysis general instrument co., LTD, TU-1810S, China). The S content was assayed by the ICP-AES (Thermo Electron Corporation, IRIS Intrepid XSP, USA). The Cu and Fe contents were determined by the atomic absorption spectrometry (Beijing sharp analysis instrument co., LTD, WFX-120, China).

3. Results and discussion

3.1. Effect of MoS_2 addition

MoS_2 with different additions (5%, 10%, 15%, 20%, 25% and 30%) well mixed with white matte and placed into the corundum crucible to melt at 1250 °C. After cooling, the melt blend was weighed and analyzed. The mass loss and melting status were listed in Table 2, the XRD of samples 1–4# was showed in Fig. 2 and its composition was listed in Table 3.

From Table 2, the mass loss of these samples was small and kept at 1.5%. The part of mass loss was due to the oxidation of copper matte and molybdenite. Therefore, it can be considered that the oxidation of melt was small during the process of rising temperature or preserving heat. Sample 1# was melted completely, and samples 2–6# had obviously stratified phenomenon. Especially to the samples 5# and 6#, only the outermost layer closed to a crucible was melted to form the compact solid solution, and the center of melt was not melted and only was sintered slightly. The bottom part of samples 2–4# and the melted part

Table 1
The composition of white matte.

Element	Cu	S	Zn	Fe	Pb	O
Content/%	77.72	17.57	0.084	0.638	0.519	2.88

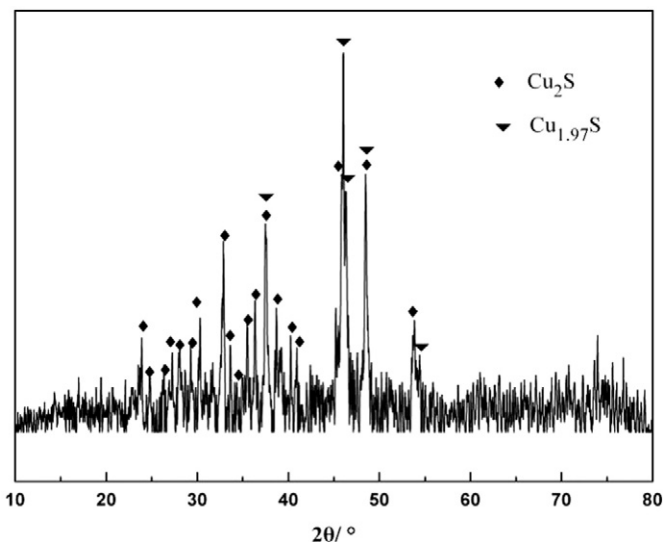


Fig. 1. The XRD pattern of white matte.

of samples 5 ~ 6# were the compact off-white tiny particle with metallic cluster. The upper part of samples 2–4# was black.

From Fig. 2a, the XRD patterns showed that $\text{Cu}_{1.96}\text{S}$, MoS_2 and MoO_2 were the main phase for the upper part of samples 2–4#. With increasing MoS_2 addition, the diffraction peak intensity of MoO_2 and MoS_2 increased, which accorded with the results listed in Table 2. From the XRD patterns in Fig. 2b, the main phase of bottom part of samples 1–4# was Cu_2S ($\text{Cu}_{1.96}\text{S}$) and MoS_2 . The diffraction peak intensity of MoS_2 also increased with the increase of MoS_2 addition. Because the upper melt can contact with air, part of MoS_2 was oxidized into MoO_2 (in Fig. 2a). It was not suitable to investigate the dissolving status of molybdenite. On the contrary, the bottom melt cannot contact with air. Therefore, the bottom melt was used to research the dissolving status of molybdenite in matte. From Fig. 2, it can be seen that molybdenite entered into matte mainly in the form of MoS_2 , which accorded with the report of reference [15].

From Table 3, as the MoS_2 addition was 0–20%, the MoS_2 content in the matte also increased with increasing MoS_2 addition. However, the MoS_2 content of matte phase calculated according to the Mo content of sample was below the MoS_2 addition. Obviously, it is because part of MoS_2 was oxidized into MoO_2 and entered into the upper melt. The results showed that the highest MoS_2 content dissolved in matte was 14.95% under the conditions of different MoS_2 additions. To the samples with MoS_2 addition 25% and 30%, although the addition was more than 20%, the Mo content entered into melt was less and was only 2.67% and 5.86%, respectively, which was different from the dissolving law of substance in aqueous solution. In aqueous solution, if the addition of substance exceeded its solubility, the concentration of substance would keep constant. However, there was a large difference in the melting point between white matte and MoS_2 . So, as the mixture of MoS_2 and white matte was heated, the temperature first reached the melting point of white matte, and the outer white matte began to melt. The firstly formed droplet would disperse among the particles of un-melted molybdenite. With increasing amount of droplet, these droplets can

Table 2
The melting status of white matte and MoS_2 with different additions (1250 °C).

No.	Addition MoS_2 /%	Mass loss/%	Melting status
1#	5	0.96	Completely melted
2#	10	1.18	Melted, two-layer
3#	15	1.34	Melted, two-layer
4#	20	1.51	Melted, two-layer
5#	25	1.44	Melted, only outer
6#	30	2.99	Melted, only outer

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