

Study on reduction behavior of molybdenum trioxide in molten steel

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Direct alloying with molybdenum trioxide is a promising technology for steelmaking process, which has the advantages of resource-saving, cost-reducing and environment-friendly. In the present study, the reduction behavior of molybdenum trioxide in molten steel and the method to prevent volatilization of molybdenum trioxide were investigated. Molybdenum yield was measured after the reduction experiment for direct alloying with molybdenum trioxide, and the results show that the activity of reducing agents toward the MoO_3 reduction reaction decreases in the following order: Al, Si, C and Fe. Binary basicity of slag affects the reduction of MoO_3 observably at the range from 1.0 to 1.5, and meanwhile, binary basicity has little influence on yield of molybdenum when basicity is greater than 1.5. The volatilization of MoO_3 can be effectively inhibited by mixing CaO, CaCO_3 , or Fe_2O_3 . Moreover, the molybdenum yield could be up to 98% by using Fe_2MoO_4 and CaMoO_4 as precursor materials for molybdenum alloying.

Keywords: Molybdenum trioxide, Reduction behavior, Volatilization, Direct alloying

Molybdenum is one of the most important alloying elements in steel, which is unique and irreplaceable. Traditionally, the most common material for making steel containing molybdenum is ferromolybdenum, which is usually added to a ladle during steel composition adjustment. Ferromolybdenum dissolves in molten steel easily, and leads to a high yield of molybdenum. However, the major disadvantage of this material is its relatively high production cost. In view of this, molybdenum trioxide was used in steelmaking process to replace ferromolybdenum, and the application of this technology has the advantages of saving of raw materials, saving production cost and alleviating environmental problems. Many researchers¹⁻⁶ have proposed the feasibility for direct alloying with metal oxides, including manganese, chromium, vanadium and nickel. For direct alloying with molybdenum trioxide, Chen *et al.*⁷ and Guo *et al.*⁸ investigated the behavior of molybdenum trioxide in slag. It was concluded that the reduction of molybdenum oxide is a fast reaction, and the controlling of basicity of slag can prevent the oxidation loss of molybdenum. Song *et al.*^{9,10} designed a alloying method through the silicothermic self-reducing MoO_3 briquettes, and it was found that the yield of molybdenum was up to 95% by using self-reducing briquettes of MoO_3 , FeSi, CaO and CaF_2 .

The main problem for direct alloying with molybdenum trioxide is its sublimation^{11,12}, which leads to a low yield of molybdenum in steelmaking process. It has been reported by several researchers¹³⁻¹⁵ that the alkalis and alkaline earth oxides as well as carbonates can restrain the evaporation of molybdenum trioxide, since the molybdates could be formed at around 600°C which is far below clear evaporation point of molybdenum trioxide. In the present study, the reduction behavior of molybdenum trioxide in molten steel was studied. The thermodynamic calculation for reduction reaction of molybdenum trioxide and [C], [Al], [Si], [Fe] was carried out, and the molybdenum yield was measured after the reduction experiment for direct alloying with molybdenum trioxide. The major effects on Mo yield investigated in this study included the reductive agents, inhibitors for MoO_3 , feeding methods, target molybdenum content as well as basicity of slags.

Experimental Study

Materials

The activated carbon (purity≥99%), silicon powder (purity≥99%), aluminum powder (purity≥99%) and iron powder (purity≥98%) were used as reducing agents, and the calcium oxide (purity≥98%), magnesium oxide (purity≥99%), calcium carbonate (purity≥98%), ferric oxide (purity≥99%) were used as inhibitors. These powders were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd..

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Before the experiment, calcium oxide and magnesium oxide were preheated at 900°C for 12 h to remove residual H₂O, and molybdenum trioxides (particle size -150 and +106 μm, purity ≥99%) were dried at 200°C for about 12 h. Fe₂MoO₄ used in this study was synthesized by the method proposed by Morales *et al.*¹⁶, and the product was analyzed by X-ray diffraction (XRD). As can be seen from Fig. 1, the XRD spectrum confirmed the presence of Fe₂MoO₄. The powder mixtures were prepared by thoroughly mixing in an agate mortar in stoichiometric proportions.

Experimental procedure

The experiments were carried out in a carbon tube furnace and the powder mixtures were placed in a corundum crucible with inner diameter of 90 mm and height of 900 mm. Then, the corundum crucible was lowered to the constant temperature region of the furnace. The purified nitrogen (purity ≥99.99%) with the flow rate of 2 L/min was used as the protecting gas during the experiments. The temperature of

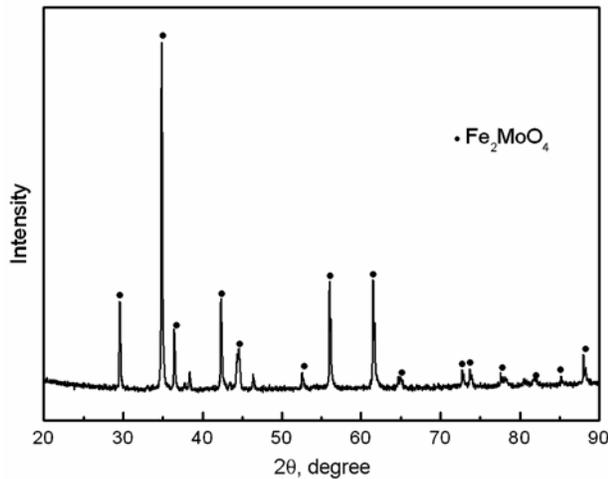


Fig. 1—XRD pattern for the synthetic iron molybdate

each reaction was measured by means of a platinum-rhodium thermocouple located just below the corundum crucible which contained the sample. The content of molybdenum of the ingot was measured after the furnace body cooling to ambient temperature.

Three different experiments were carried out to achieve the purpose of the present study. In the first experiment, the activated carbon, silicon powder and aluminum powder were mixed with molybdenum trioxide respectively, and the influences of slag basicity upon the reduction behavior were investigated. In the second experiment, the effects of feeding methods were studied, and the three different feeding methods are shown in Fig. 2. The third experiment was carried out to figure out the impacts from inhibitor, and the molybdenum trioxides mixed with CaO, CaCO₃, MgO or Fe₂O₃ were added to liquid steel and then the molybdenum content was measured after the experiment. The mixture compositions used in the third experiment are shown in Table 1. In addition, the experiments by use of MoO₃+C, CaO+MoO₃+C and Fe₂O₃+MoO₃+C were slightly different, sampling process was carried out in 2 min, 5 min, 10 min, 15 min and 20 min after reaching 1600°C.

Table 1—Compositions of alloying materials used for 500 g molten iron

No.	Compositions of materials (wt%)	Mixture mass (g)
N-1	CaMoO ₄ -84.7; C-15.3	12.3
N-2	MoO ₃ -80.0; C-20.0	9.4
N-3	CaO-23.7; MoO ₃ -51.4; C-12.9	12.3
N-4	CaCO ₃ -35.7; MoO ₃ -51.4; C-12.9	14.6
N-5	MgO-18.2; MoO ₃ -65.5; C-16.4	11.5
N-6	Fe ₂ O ₃ -16.7; Fe-23.3; MoO ₃ -5.0; C-15.0	16.7
N-7	Fe ₂ MoO ₄ -85.0; C-15.0	16.7

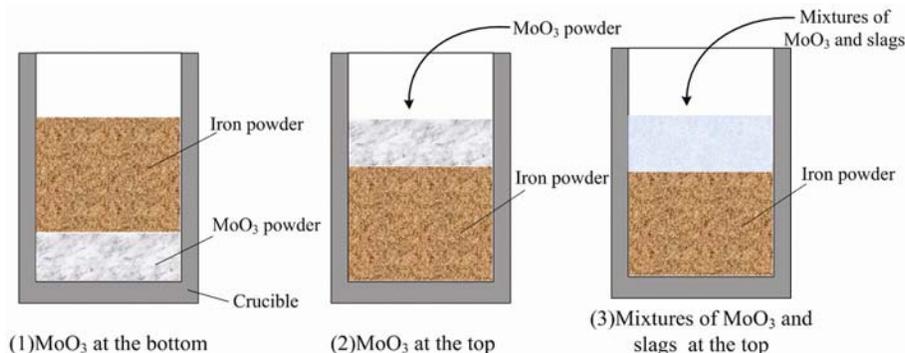


Fig. 2—Schematic diagrams of different feeding methods for MoO₃ reduction experiment

After the experiments, the molybdenum content was determined by the inductively coupled plasma-atomic emission spectrometry (ICP-AES), and based on the analysis results, the yield of molybdenum was calculated by Eq. (1):

$$\eta = \frac{[Mo]}{[Mo]_T} \times 100\% \quad \dots (1)$$

where η is the yield of molybdenum, and $[Mo]$, $[Mo]_T$ are the molybdenum content in ingots and the theoretical target molybdenum content, respectively.

Results and Discussion

Thermodynamics

The Gibbs energy change for reduction of MoO_3 in molten steel was calculated by HSC Chemistry 6.0. Due to boiling point of MoO_3 ($795^\circ C$) and its volatility, the reduction reactions between reducing agents and gas MoO_3 were calculated as well. The calculated results show that reduction reactions between MoO_3 and $[C]$, $[Si]$, $[Al]$, $[Fe]$ occur in standard state, and $[Al]$ and $[Si]$ have stronger reducing ability in comparison with $[Fe]$ at steelmaking temperature. In addition, the reducing ability of $[Al]$ and $[Si]$ increases slightly as the temperature increases further. The feasibility of $[Fe]$ reacting with MoO_3 means that MoO_3 is unstable in molten steel, even in the blowing oxygen stage in steelmaking process. Through the comparison of Gibbs energy change for reaction with MoO_3 in liquid or gas state, it indicates that reduction reaction with gas MoO_3 has a lower Gibbs energy change, and it is more reactive for gas MoO_3 . Moreover, MoO_3 bubbles improve the kinetics condition of the reaction between reducing agents and MoO_3 in the process of MoO_3 bubbles rising.

Effects of reducing agents

The influence of different reducing agents on the yield of molybdenum is as shown in Fig.3. It can be observed that the reducing agents have significant influence on the molybdenum yield. The molybdenum yield is lower without reductant, since the reduction reaction between Fe and MoO_3 could not occur before the melting of iron powder. Even so, the final molybdenum yield in the case of without reductant almost reaches to 90% compared to Si, Al, C as the reducing agents. Using a reducer of Al, Mo yield reaches up to 96%, and the reason might be strong reducing ability and low melting point of aluminum. Aluminum powder melts with temperature rising

which provides a good kinetic condition. Moreover, molybdenum trioxide could not be reduced effectively by Si before the melting of iron powder. Conversely, Si reduces molybdenum trioxide strongly when Si melts into molten steel.

Effects of basicity

Different reducing agents mixed with MoO_3 were added to molten steel with three levels of basicity, and the molybdenum yields are shown in Fig. 4. Judging from the results, molybdenum exhibits a high yield with carbon as reducing agent in lower basicity stage compared to Al and Si. As the basicity rises, the reducibility of Al and Si is further improved, and when basicity reaches to 1.5, the molybdenum yield is gradually stabilizing. Conversely, the reducibility of carbon decreases with higher basicity. The reason is

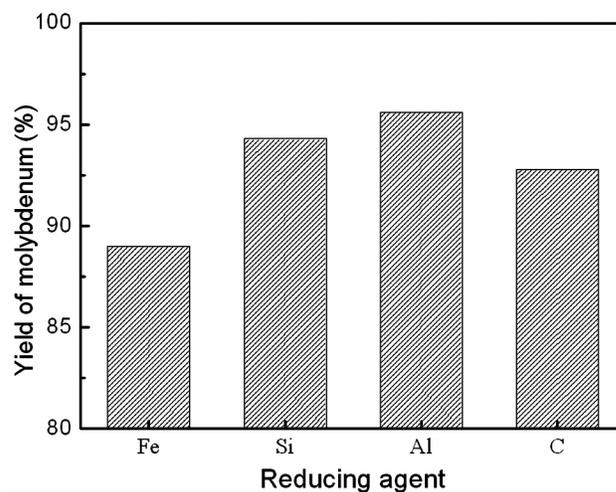


Fig.3—Effects of reducing agents on the yield of molybdenum

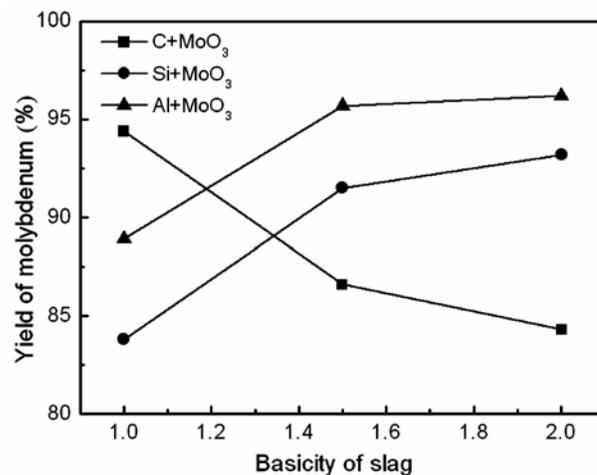


Fig. 4—Effects of slag basicity on the yield of molybdenum

lower basicity slag contains more SiO_2 , which prevents the reaction between MoO_3 and Si, Al. More importantly, MoO_3 is hard to be combined with CaO for low basicity slag, and in that case the volatilization of MoO_3 could result in a lower Mo yield.

Effects of feeding methods

The molybdenum yields with three different feeding methods are shown in Fig. 5. It is observed that Mo yield is very low when MoO_3 was added to the molten steel from the top of crucible, and the reason is the volatility of MoO_3 after MoO_3 being dropped to surface of molten steel. When MoO_3 was placed to the bottom of crucible covered with iron powder, MoO_3 is hard to volatilize as temperature rises. The molybdenum trioxide was protected by the upper iron powder, which causes a higher molybdenum yield being up to 95%. For the third feeding method, MoO_3 was added to liquid steel mixed with slag and reducing agent. MoO_3 reacts with CaO from slag, and then, the volatilization of MoO_3 decreases. As a result, molybdenum yield reaches to 90%.

Effects of target molybdenum content

In the case of direct alloying without any reducing agent in molten steel, the molybdenum yields are shown in Fig. 6. The target molybdenum content are 0.5%, 1%, 2% and 3%, respectively. The results of this experiment confirm that the molybdenum trioxide could be reduced by [Fe] in molten steel, one step further, Mo yield decreases with target molybdenum content increasing. The reason is that larger target Mo content requires more MoO_3 which is more volatile in steelmaking process. From this point, it can be concluded that it is a highly effective way to smelt

low molybdenum content alloy steel relative to high molybdenum content alloy steel.

Effects of inhibitor

The direct alloying experiments of molybdenum trioxide mixed with CaO, CaCO_3 , MgO or Fe_2O_3 were carried out at 1600°C , and in the meantime, experiments of CaMoO_4 and Fe_2MoO_4 in the place of MoO_3 were performed. The yields of molybdenum are shown in Fig. 7. Direct alloying with CaMoO_4 and Fe_2MoO_4 have higher molybdenum yield being up to 98% for their high temperature stability. The mixture of MoO_3 and C without adding other oxides leads to a lower molybdenum yield which is 93.3%. Molybdenum trioxide becomes more stable for reacting with CaO, CaCO_3 and Fe_2O_3 in the alloying process. As a result, molybdenum yield reaches to a higher level. However, it's worth noting that the mixture of $\text{MgO}+\text{MoO}_3+\text{C}$ leads to the lowest Mo yield of 82.6% in this experiment. MgMoO_4 is unstable in slag compared to CaMoO_4 and Fe_2MoO_4 , though MoO_3 and MgO combine to MgMoO_4 as the temperature rises. At high temperature, MgMoO_4 decomposes into MgO and MoO_3 , which leads to the low molybdenum yield.

During the experiments of MoO_3+C , $\text{CaO}+\text{MoO}_3+\text{C}$ and $\text{Fe}_2\text{O}_3+\text{MoO}_3+\text{C}$, the samples were taken at 2 min, 5 min, 10 min 15 min and 20 min after 1600°C , respectively, and the results are shown in Fig. 8. The reduction reaction rates in this experiment are all in high level, and the molybdenum yields could reach to about 90% at 10 min. After 10 min of adding mixtures to molten steel, the reaction rate becomes stable. The molybdenum yield of MoO_3+C is up to 60% at 2 min and above 80% at

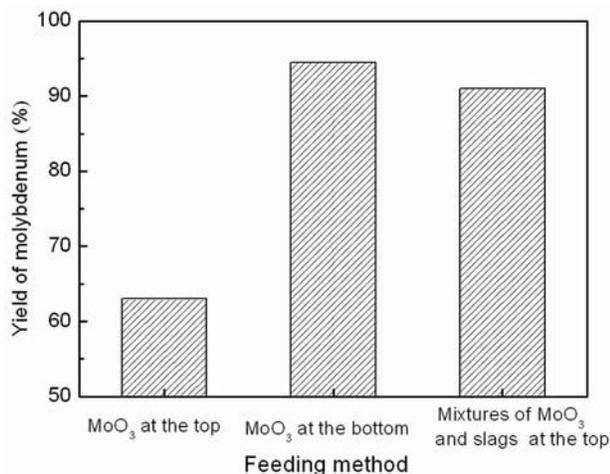


Fig. 5—Effects of feeding methods on the yield of molybdenum

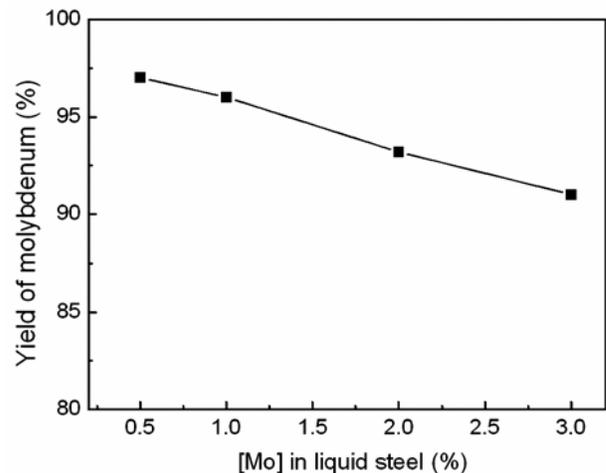


Fig. 6—Effect of [Mo] on the yield of molybdenum

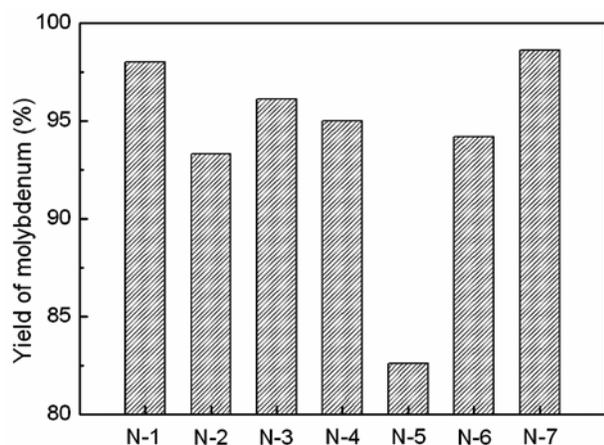


Fig. 7—Effects of inhibitors on the yield of molybdenum

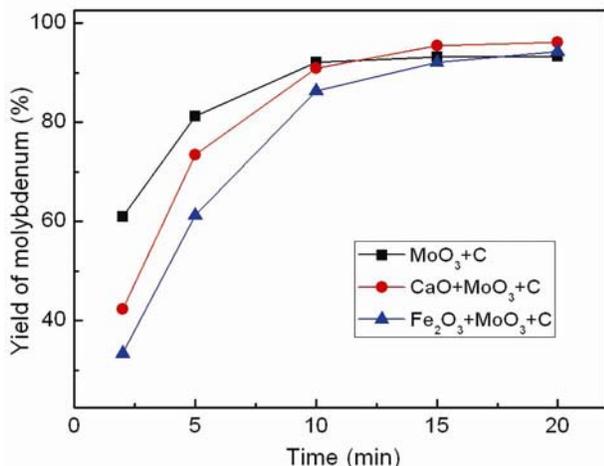


Fig. 8—Relationship between Mo yield and time

5 min. In the same time, the mixtures of CaO+MoO₃+C and Fe₂O₃+MoO₃+C have lower reaction rate, and the molybdenum yields only reach to the range of 60% and 70%. The main reason for the above-mentioned phenomena is that the compound reactions took place between MoO₃ and CaO, Fe₂O₃ in alloying process, and the compound reaction products are more stable than MoO₃. Moreover, the molybdenum yield is stable after 10 min. From the results, it is observed that molybdenum yield with mixture of MoO₃+C is lower at 20 min, however, mixture of CaO+MoO₃+C and Fe₂O₃+MoO₃+C lead to high Mo yield which are 96.1% and 94.2%. The causes for different Mo yields remain attributed to the inhibiting effects from CaO and Fe₂O₃.

Conclusions

In the present study, the reduction behaviors of molybdenum trioxide mixed with different reducing agents and inhibitors in molten steel

were investigated. Some important findings are summarized as follows:

It is feasible to reduce MoO₃ by [Fe] in molten steel without other reducing agents, and the activity of reducing agents toward the MoO₃ reduction reaction decreases in the following order: Al, Si, C and Fe.

The basicity ranging from 1 to 1.5 has obvious influence on the reduction of MoO₃. However, the molybdenum yield tends to be stabilized while the slag basicity is greater than 1.5. Conversely, the reducibility of carbon decreases with basicity rising.

CaO, CaCO₃, and Fe₂O₃ can restrain volatilization of MoO₃ effectively, and CaO is the most effective inhibitor. The mixing of MoO₃ with CaO, CaCO₃ or Fe₂O₃ in direct alloying process could be an effective approach to obtain high molybdenum yield. In addition, the direct alloying with CaMoO₄ or Fe₂MoO₄ as precursor has a higher molybdenum yield being up to 98% for their high-temperature stability.

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