Metallurgical and Materials Engineering *Scientific paper*
Association of Metallurgical Engineers of Serbia AMES *https://doi.org/10.30544/346*

A STUDY ON DIRECT ALLOYING WITH MOLYBDENUM OXIDES BY FEED WIRE METHOD

Jingjing Zou[1], Hangyu Zhu[1,2], Jian Sun[1], Jigang Liu[3] and Jixuan Zhao[2]*

[1] Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan-430081, China.
[2.] Hubei Provincial Engineering Technology Research Center of Metallurgical Secondary Resources, Wuhan University of Science and Technology, Wuhan-430081, China.
[3.] Special Steel Plate Steelmaking Plant, Xingcheng Special Steel Co Ltd, Jiangyin-214400, China.

Received 20.03.2018
Accepted 21.03.2018

Abstract

Direct alloying with molybdenum oxides has been regarded in years; the main addition methods are adding to the bottom of electric arc furnace (EAF) with scrap, adding to the ladle during the converter tapping and mixing molybdenum oxide, lime and reductant to prepare pellet added to basic oxygen furnace (BOF). In this paper, a new method for direct alloying with molybdenum trioxide is proposed, adding molybdenum trioxide molten steel by feeding wire method in ladle furnace (LF) refining process. The feasibility of molybdenum oxide reduction, the influence rules of bottom-blown on liquid steel fluidity and the yield of molybdenum by feeding wire method were analyzed. Results show that molybdenum oxide can be reduced by [Al], [Si], [C], and even [Fe] in molten steel. Bottom blowing position has a significant influence on the flow of molten steel when the permeable brick is located in 1/2 radius. The yields of Mo are higher than 97% for the experiments with feed wire method, the implementation of direct alloying with molybdenum trioxide by feed wire method works even better than that uses of ferromolybdenum in the traditional process.

Keywords: Molybdenum oxides; Direct alloying; Feed wire method; Yield of molybdenum.

---

* Corresponding author: H. Y. Zhu, *zhuhy1984@sina.com*

Introduction

Direct alloying with oxide in steelmaking process is a new alloying method relative to traditional process; oxide minerals added to smelting furnace react with reductants in molten steel, the metal elements are as reduction product dissolved in molten steel [1-3]. The technology of direct alloying with oxide has developed rapidly in recent years, and the proposed method has been applied to chrome ore, manganese ore, nickel oxide, scheelite, molybdenum oxide, niobium oxide and vanadium slag [4-7]. The implementation of the process can reduce the production cost, protect the environment and improve the economic profits and social benefits.

Many researchers have investigated direct alloying with molybdenum oxide in steelmaking – the central research focuses on volatilization of molybdenum trioxide and adding method. Molybdenum trioxide has a very high activity due to a melting point of 795 ℃; it will be volatile at the temperature higher than 700 ℃ and result in a lower yield of molybdenum [8]. The most effective solution is mixing lime, which is used as an inhibitor, with molybdenum trioxide [9]. Moreover, the melting process of direct alloying was studied, and the primary addition method is as follows, adding to the bottom of EAF with scrap, adding to the ladle during the converter tapping, molybdenum oxide, lime, and reductant are mixed to prepare pellet added to BOF [10-12]. Based on previous researches and practical experiences, a new method for direct alloying with molybdenum trioxide is proposed in this paper; molybdenum trioxide can be added to molten steel by feeding wire method in LF refining process.

Materials and methods

Simulation parameters

According to the 40 t ladle furnace for industrial experiment, the influences of blowing position and flow rate of argon gas on liquid steel fluidity were studied by using FLUENT software., the purpose of simulation is to gain the process parameters of blowing argon, and provide a theoretical basis for direct alloying with molybdenum oxide by wire feeding method. The bottom and top diameters are 2150 mm and 2300 mm, respectively. Molten steel level is 1600 mm with 40 t molten steel; these physical dimensions are shown in Figure 1. Variable technological parameters are argon blowing position and the argon flow rate. Argon blowing position is located in the 1/3 radius, 1/2 radius and the ladle center, meanwhile, the argon flow rate is set to 8 m^3/h, 12 m^3/h, and 15 m^3/h, respectively.

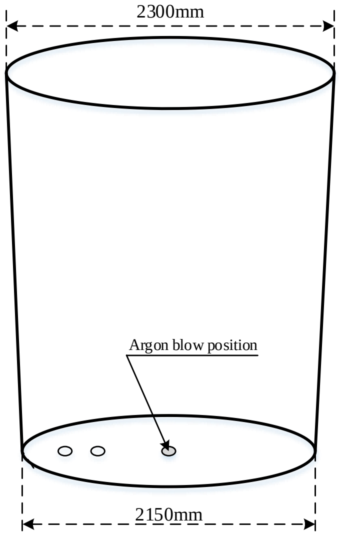


Fig. 1. Dimensions and argon blow positions for 40t ladle furnace.

Smelting process for the industrial experiment

In this study, the steelmaking process is EAF→LF→VD→Casting→ESR, and the direct alloying with feeding wire method was taken in the LF refining process, as shown in Figure 2. Three kinds of steel were selected in the industrial experiment; the steel chemical compositions are shown in Table 1.

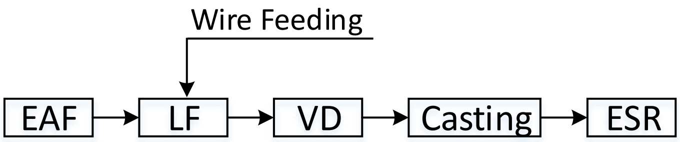


Fig. 2. Process for direct alloying with molybdenum trioxide by feeding wire method.

Table 1. The composition of steels for the industrial experiment.

Steel grade	C	Si	Mn	Cr	Mo	P≤	S≤
MC3-2	0.78-0.82	0.70-0.80	0.60-0.80	3.00-3.20	0.50-0.60	0.015	0.015
MZ5-3	0.61-0.67	1.05-1.20	0.35-0.50	5.10-5.40	1.01-1.21	0.018	0.008
20MnSiMo	0.17-0.23	0.40-0.70	1.30-1.70	<0.03	1.00-1.20	0.020	0.020

Raw material

Molybdenum oxides used in this study were supplied by Hunan Shizhuyuan Nonferrous Metals CO., LTD. The elemental quantitative analysis was carried out using chemical analysis method, the content of molybdenum was 44.24%. The chemical composition of industrial molybdenum oxides is shown in Table 2. Subsequently, X-ray diffraction (XRD) was used to measure the composition of molybdenum oxides, the primary chemical constituents are MoO_3 and MoO_2, which is shown in Figure 3.

Table 2. The chemical composition of industrial molybdenum trioxide.

Element	Mo	Si	Ca	Cu	P	S
Content, %	44.24	4.30	2.16	0.13	0.013	0.15

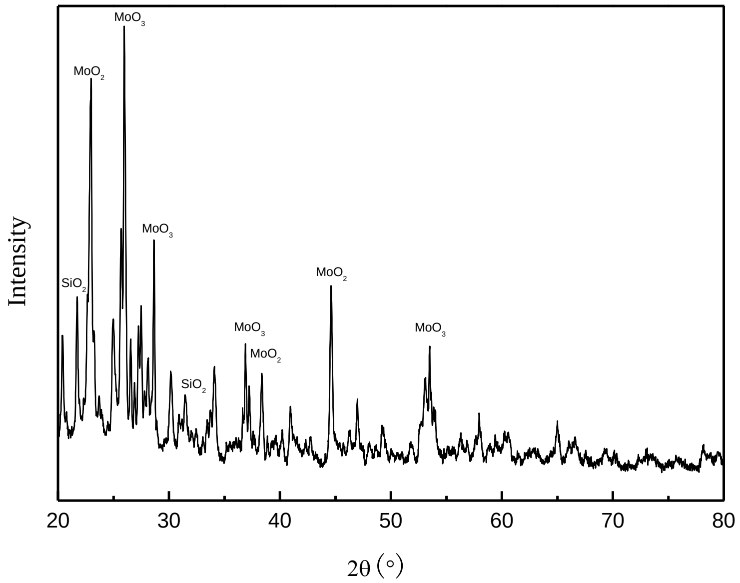


Fig. 3. X-ray diffraction pattern for industrial molybdenum trioxide

The calculation method of Molybdenum yield

The steel samples were obtained before adding molybdenum oxide to molten steel, and the amount of molybdenum oxide was calculated based on the Mo content of samples obtained. At the end of LF refining, the Mo content of steel samples was analyzed, and the yield of Mo was calculated using the following equation:

$$\eta_{Mo} = \frac{\Delta m_{[Mo]}}{m_{(Mo)}} = \frac{m_{[Mo]e} - m_{[Mo]i}}{m_{(Mo)}} \quad (1)$$

$\Delta m_{[Mo]}$- the increment of Mo metal in molten steel, kg;
$m_{(Mo)}$- the pure Mo metal quantity from molybdenum oxide, kg;
$m_{[Mo]i}$- the Mo metal quantity before direct alloying, kg;
$m_{[Mo]e}$- the Mo metal quantity after direct alloying, kg.

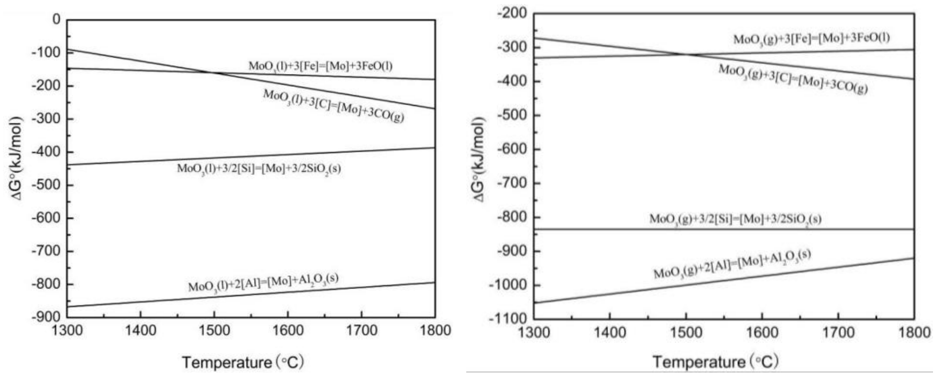
Results and discussion

Thermodynamics

There are multiple elements in molten steel, such as Si, Al, C, and so forth. Most important is Fe makes up a high proportion of molten steel and reduction reaction could occur between [Fe] and MoO_3. Gibbs energy reduction of MoO_3 in molten steel was calculated using HSC Chemistry 6.0, results and chemical reaction equations are shown in Table 3. Since the melting point of molybdenum trioxide is 795 ^{o}C and the boiling point is 1155 °C and its volatility, reduction reaction between reducing agents and gas MoO_3 was calculated as well. The relationship between Gibbs energy and temperature are shown in Table 3 and Figure 4.

Table 3. Gibbs energy of MoO_3 reduction in molten steel.

No.	Reaction equations	ΔG^o (kJ/mol Mo)
1	$MoO_3(l)+2[Al]=[Mo]+Al_2O_3(s)$	$-1018.44+0.147T$
2	$MoO_3(g)+2[Al]=[Mo]+Al_2O_3(s)$	$-1323.1+0.264T$
3	$MoO_3(l)+3/2[Si]=[Mo]+3/2SiO_2(s)$	$-543.63+0.103T$
4	$MoO_3(g)+3/2[Si]=[Mo]+3/2SiO_2(s)$	$-834.87+0.220T$
5	$MoO_3(l)+3[C]=[Mo]+3CO(g)$	$281.1-0.360T$
6	$MoO_3(g)+3[C]=[Mo]+3CO(g)$	$-23.56-0.242T$
7	$MoO_3(l)+3[Fe]=[Mo]+3FeO(l)$	$-76.11-0.068T$
8	$MoO_3(g)+3[Fe]=[Mo]+3FeO(l)$	$-380.77+0.049T$



(a) *(b)*

Fig. 4. Gibbs energy versus temperature for reduction of (a) liquid MoO_3 and (b) MoO_3 gas

From Figure 4, It is observed that reduction reactions occur between MoO_3 and [C], [Si], [Al], [Fe] in the standard state. [Al] and [Si] have the stronger reducing ability when compared to [Fe] a steelmaking temperature; also, reducing the 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 the steelmaking process. Through comparison of Gibbs energy for reaction with liquid and gas MoO_3, it indicates that reduction reaction with gas MoO_3 has a lower Gibbs energy, and it is more reactive for gas MoO_3. Moreover, MoO_3 bubbles improve kinetics condition of reaction between reducing agents and MoO_3 in the process of MoO_3 bubbles rising.

Simulation results for wire feeding method

According to the 40 t ladle furnace for the industrial experiment, the influences of blowing position and flow rate of argon gas on liquid steel fluidity were studied by using the FLUENT software. The purpose of the simulation is to gain the process parameters of blowing argon and provide a theoretical basis for direct alloying with molybdenum oxide by wire feeding method. Argon blowing position is located in the 1/3 radius, 1/2 radius and the ladle center, meanwhile, the argon flow rate is set to $8m^3/h$, $12m^3/h$, and $15m^3/h$, respectively.

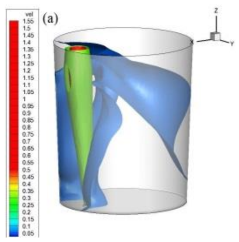
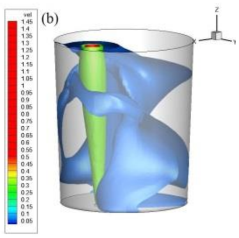
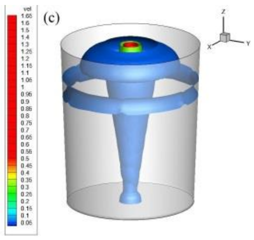
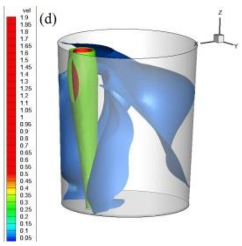
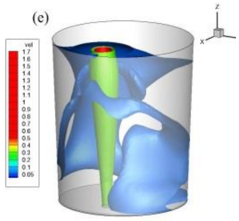
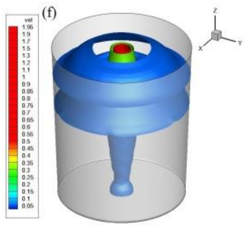
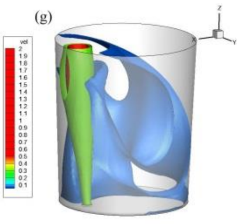
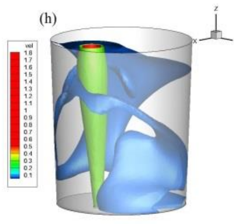
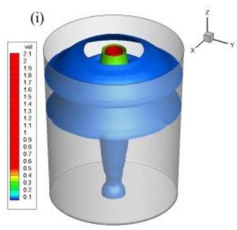
Parameters	1/3 radius	1/2 radius	Ladle center
$8m^3/h$			
$12m^3/h$			
$15m^3/h$			

Fig. 5. Liquid steel flow rate versus argon flow rate and blowing position

The flow characteristics of liquid steel are described in Figure 5. Liquid steel movement is more symmetrical, and the flow rate is below 0.05 m/s with a relatively large zone (blue region), when argon blowing position is in the ladle center. Changing the position of permeable brick and flow rate of argon leads to a small area change of liquid steel flow rate with 0.3 m/s and 0.5 m/s, corresponding to green and red regions. If the argon blowing position is fixed, the liquid steel flow peak changes with varying argon flow rate range of 8~15 m^3/h. However, the other liquid steel flow regions have no significant change, that means the effect of argon flow rate on the fluidity of liquid steel is not evident at the specific scope of argon flow rate.

Figure 5 (a, d, e) shows that the local flow rate near the ladle wall is more significant than the center, which will make the refractories be eroded severely from molten steel washout, and the reason is that argon blowing position is too close to the ladle wall. As a result, the service life of refractories is reduced dramatically. On the other hand, the cleanness of molten steel will be decreased because of the refractory loss.

Reasonable argon blowing region can ensure a molten steel flow fully, reduce the dead region volume in the LF refining process, and reduce the refractory erosion from flowing molten. When the permeable brick is located in the 1/2 radius (b), the high-speed fluid flow region is far from the ladle wall, which can stir molten steel well. Therefore, the argon blowing position located to 1/2 radius (b) is good for the reduction reaction between molybdenum trioxide by using of feeding wire method and elements in liquid steel.

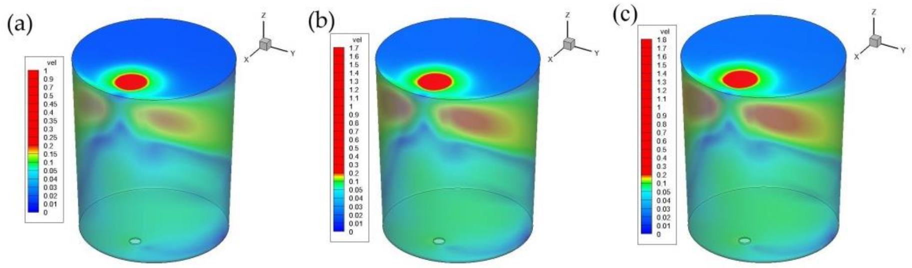


Fig. 6. Liquid steel flow rate characteristic with argon blow of (a) 8m^3/h, (b) 12m^3/h and (c) 15m^3/h located to 1/2 radius

If the argon flow is higher than a particular value in the blowing process, the liquid steel flow rate on the top of molten steel would be more significant. Molten steel is exposing to the atmosphere, which is harmful to direct alloying with molybdenum trioxide. Therefore, an optimal argon flow range should be set in LF refining process. The fluctuation of top liquid steel and the molten steel flow characteristic in ladle furnace were studied aiming to determine a reasonable argon flow parameter, while argon blow position was located to 1/2 radius (b). The liquid steel fluctuation at top and wall of ladle furnace are shown in Figure 6.

Figure 6 shows that the liquid steel flow rate at the most region of ladle furnace does not increase naturally with the increase of argon flow. The most significant liquid steel flow rate increases, however, the increasing amplitude (1.6-1.8 m/s) is lower, and the fast movement region is small (red region). Therefore, the argon blowing amount has no apparent effects on the top liquid steel fluctuation, and top molten steel covered with slag would not be exposed to the atmosphere at the argon blowing range of 8-15m^3/h. In conclusion, the permeable brick is located to 1/2 radius and increase argon blowing rate suitable can improve the gas-liquid flow field and would be conducive to optimize metallurgical quality.

Table 4. Chemical compositions of steel samples for smelting MC3-2.

No.	C	Si	Mn	P	S	Cr	Ni	Mo	V	Cu
1	0.24	0.00	0.02	0.007	0.024	0.006	0.16	0.14	0.00	0.08
2	0.06	0.08	0.01	0.005	0.024	0.24	0.17	0.44	0.00	0.10
3	0.41	0.38	0.05	0.006	0.014	1.5	0.17	0.47	0.01	0.10

Results of the industrial experiment

In the process of MC3-2 smelting, Sample 1 was analyzed, and the content of [Mo] is 0.14%, before adding molybdenum oxide. Ten minutes after adding molybdenum oxide to molten steel, Sample 2 was analyzed, and the content of [Mo] is 0.44%. After the slag was melted entirely, steel Sample 3 was taken, the content of [Mo] for Sample 3 is 0.47%, as shown in Table 4.

The Mo yield smelting MC3-2 of the industrial experiment was calculated by Equation 1, based on Table 4, and the final Mo yield is 98.43%. Most reduction reaction takes place quickly after the feeding wire process, because of the high activity of molybdenum trioxide. The molybdenum in the slag is in the form of molybdenum trioxide, which is favorable for the reduction reaction in slag.

Table 5. Results of molybdenum content for the industrial experiment.

Steel	$[Mo]_I$, %	$[Mo]_e$, %	η_{Mo}, %
MC3-2	0.14	0.47	98.43
MZ5-3	0.06	0.51	98.41
MZ5-3	0.19	0.58	97.87
20MnSiMo	0.22	0.99	97.27
Average yield, %			98.00

Also, four industrial experiments were carried out in this study, the initial Mo content and the steel grade were changed, and the results are shown in Table 5. The yields of Mo are higher than 97% for the experiments with feed wire method, the implementation of direct alloying with molybdenum trioxide by feed wire method works even better than that uses of ferromolybdenum in the traditional process.

Conclusions

Molybdenum oxide has a very high activity and can be reduced by [Al], [Si], [C], in molten steel, moreover, [Fe] reacts with molybdenum trioxide. [Mo] as reaction production reaches into the molten steel. Bottom blowing position has a significant influence on the flow of molten steel; the better stirring effect is beneficial to the reaction between molybdenum trioxide and liquid steel elements when the permeable brick is located within 1/2 radius. The proper increase of argon flow rate is conducive to the improvement of the gas-liquid flow field and the metallurgical reaction. Molybdenum oxide alloying reduction process mainly occurs in liquid steel, the yields of Mo are higher than 97% for the experiments with feed wire method, the implementation of direct alloying with molybdenum trioxide by feed wire method works even better than that uses of ferromolybdenum in the traditional process.

Acknowledgments

This work was supported by the Technology and Innovation Fund of Wuhan University of Science and Technology (17ZRA007).

References

[1] Z. B. Li, H. Y. Zhu, H. S. Yang: J Iron Steel Res, 25 (2013) 1-3.
[2] Z. Janjušević, V. Matković, M. Bugarčić, M. Sokić, B. Marković, V. Manojlović, Zaštita Materijala, 59 (2018) 100-107.
[3] H. Zhu, J. Li, Z. Xue, W. Wang: Indian J Eng Mater Sci, 22 (2015) 460-464.
[4] T. Takaoka, Y. Kikuchi, Y. Kawai, In: Proceedings ISFNAP'90, Hamilton, Ontario, 1990, p.164.
[5] T. Takaoka, I. Sumi, Y. Kikuchi, Y. Kawai: ISIJ Int, 33 (1993) 98-103,
[6] Z. B. Li, P. M. Guo, G. W. Lin, H. S. Zhang: China Tungsten Industry, 15 (2000) 26-29.
[7] Z. B. Li, P. M. Guo, H. S. Zhang, G. W. Lin: Iron Steel, 34 (1999) 20-23.
[8] T. V. Charlu, O. J. Kleppa, J Chem Thermodyn: 3 (1971) 697-700.
[9] H. Y. Zhu, R. Gao, W. T. Jin, L. W. Qiu, Z. L. Xue: Rare Met, 4 (2015) 1-4.
[10] J. Ying, Y. M. Gao, T. Xing, G. L. Wu: Chinese J Process Eng, 9 (2009) 12-16.
[11] D. Ma, P. M. Guo, J. M. Pang, P. Zhao: Iron Steel, 49 (2014) 19-23.
[12] H. M. Wang, Y. Li, X. J. Fan, G. R. Li: Adv Mater Res, 1095 (2015) 766-769.