METALOTHERMIC REDUCTION OF MOO₃ THROUGH MAKING NI-MO ALLOYS BY ESR METHOD

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ABSTRACT
In this research an electro slag remelting process for metalothermic reduction of molybdenum trioxides by aluminum and silicon is described. The Process uses fine MoO₃ scrap as a raw material. After melting of nickel electrode, molybdenum is alloyed with nickel by direct reduction of MoO₃ added to the slag. A mixture of aluminum and silicon can be used as reductant and the reduction is carried out in situ in the molten slag. Nickel-molybdenum ingots containing up to 33.7-wt% of molybdenum were produced by this process. The results show that Al-50%Si is a suitable compound for reduction of MoO₃ and by using proper amount of reductants, flux and charge, high efficiency of reduction will be achieved; as the mean efficiency in these experiments was 92%.

INTRODUCTION
Molybdenum and its alloys have many favorable high temperature properties and therefore they are widely used in the electronics, chemical and metallurgical industries. Molybdenum has a low capture cross-section for thermal neutrons, and is one of the most promising refractory metals for resistance against liquid metals corrosion [1,2].
The common method for making Ni-Mo alloys is using pure molybdenum and nickel, melting them with electron beam and alloying them together [3]. Solubility of nickel in molybdenum is limited but Mo could be solved up to %35 in Ni, and form three intermetallic compounds: Ni₄Mo (?), Ni₃Mo (?), NiMo (?) [4].
There has been a growing interest in producing molybdenum metal from its oxides and sulphides. For reduction of molybdenum trioxides, aluminum seems to be more suitable
than calcium and magnesium because of having lower melting point, higher heat of reduction per mole of MoO₃, and lower cost [5, 6].

Although aluminum has more tendency to reduce MoO₃ than silicon but as it has been reported that Al-50%Si has more molybdenum yield than pure aluminum [7].

The reduction of MoO₃ by aluminum and silicon takes place by the following reactions:

\[
\text{MoO}_3 + 2\text{Al} \rightarrow \text{Mo} + 2\text{Al}_2\text{O}_3 \tag{1}
\]

\[
\text{MoO}_3 + \frac{3}{2}\text{Si} \rightarrow \text{Mo} + \frac{3}{2}\text{SiO}_2 \tag{2}
\]

\( \Delta G^\circ \) for the first reaction is -30952J and for the second is -16666J. These reactions are strongly exothermic and do not need extra heating [6].

The electro slag refining process is a secondary refining method with the ability of making dense, clean and pure products [8-10]. Although ESR method is commonly used for refining metals but it has the grate capability for making different alloys with a high purity as well [11].

In this research reduction of MoO₃ by aluminum and silicon and consequently alloying of reduced molybdenum with molten nickel has been investigated.

**EXPERIMENTAL PROCEDURE**

An electro slag-remelting furnace of 400kVA capacity using a nickel electrode (50 mm diameter) with a refractory metallic mould was used in this work. An arc was stock between the nickel electrode and metallic mould to start the process. Typically 1.5 kg of slag with the composition of 38% CaF₂, 30% CaO, 17% Al₂O₃, 12% SiO₂ and 2% Al₂O₃ was initially charged in to the mould for all operations. In each experiment a particular amount of MoO₃ scrap and Al-50%Si powder, which was grinded to -50# with 10% in weight of CaO+CaF₂, were mixed together completely and pressed as cylindrical tablets with 8 cm diameter and 2 cm height. After melting all the slag, these tablets were charged into the gap between the electrode and the mould one by one.

Once the entire nickel electrode was melted, all the MoO₃ had been reacted with Al and Si and then molybdenum was completely alloyed with molten nickel.
The temperature was constant in all experiments (1200 °C) and the time from the first arc to the end of operation was about 10 minutes. After finishing all the reactions, the molten metal together with liquid slag were poured into another mould and was allowed to be solidified. The slag covered the melt and protected the metal from atmospheric oxidation. After solidification of the metal, drillings were taken from the ingots for EDX and XRF, and the slag of each experiment were prepared for the atomic absorption analysis.

**Results and discussion**

The EDX and XRF analysis determined the exact compositions of the metallic phases, which are shown in table 1. These results show that the produced ingots by this method contain molybdenum up to a maximum of 33.7%, while the maximum solubility of Mo in Ni is 35%.

It could be also seen from table 1 that the amount of silicon solved in metallic phase is much more than aluminum, and this could be attributed to Ellingham-Richardson diagram, in which the oxidation line of Al is lower than Si that means silicon reaction starts after finishing the reaction of aluminum.

Throughout five experiments in this research, MoO3 with the weight of 127, 236, 375, 577 and 4450g were charged into the ESR mould and the weight of reduced molybdenum were 79.8, 162, 224, 343 and 3960g respectively.

By division of the weight of reduced molybdenum to weight of Mo in the initial MoO3, efficiencies of the reduction calculated as 95%, 93%, 91%, 90% and 89% respectively.

So the mean efficiency in five experiments was 92% which shows the great ability of this method for reduction of MoO3.

The Al2O3 and SiO2 formed by reactions 1 and 2 are quickly solved in the slag and this facilitates the reactions to move forward. By increasing the amount of Al2O3 and SiO2 in the slag the reduced molybdenums increased as well which are shown in figures 1 and 2.

**CONCLUSIONS**

Metalothermic reduction of MoO3 and simultaneously alloying of reduced molybdenum in molten nickel in ESR furnace was studied in this research. Different amounts of MoO3
with weights of 127 to 4450g were reduced with the mean efficiency of 92%. This method has also the ability of alloying reduced molybdenum in molten nickel up to 33.7% in solid state while the maximum solubility of Mo in Ni is 35%.

Al-50%Si is suggested as the preferred reductant agent with high efficiency. The amount of silicon solved in metallic phase is much more than aluminum which shows aluminum more active in metalothermic reductions than silicon. Increasing in the amount of Al2O3 and SiO2 solved in slag facilitates the metalothermic reactions to move forward and increases the reduction of molybdenum.

Although the electro slag technique is generally used for secondary refining process, but it has a great ability for reduction of metal oxides and production of different alloys as well.

REFERENCES


8. B. E. Paton, and B. I. Medovar, Electro-slag remelting, engineering materials and design, V. 5, 10, Oct. 1962, P. 718-723


Figures:

Figure 1. Wt% Al2O3 in final slag for each experiment

Figure 2. Wt% SiO2 in final slag for each experiment

Table 1: Composition of the metallic phase

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<th>Experiment Number</th>
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