Preparation of Low-Oxygen Mo Ingot by Optimizing Hydrogen Reduction and Subsequent Melting from MoO₃

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In this study, we prepared low-oxygen molybdenum ingot through optimized hydrogen reduction by preparing the metal powder and repeatedly applying vacuum arc melting. We determined the optimal heat treatment conditions for hydrogen reduction and oxygen content lowering and obtained molybdenum metal powder with 3,000 ppm of oxygen. The obtained molybdenum powder was converted into an ingot with low oxygen contents (<100 ppm) through repeated vacuum arc melting. The molybdenum ingot thus prepared can be used as raw material for sputtering targets. [doi:10.2320/matertrans.M2012305]

(Received August 31, 2012; Accepted November 12, 2012; Published January 19, 2013)

Keywords: molybdenum, hydrogen reduction, MoO₃, oxygen, vacuum arc melting

1. Introduction

Molybdenum (melting point: 2,893 K) is a refractory metal similar to tungsten, with a low coefficient of thermal expansion and high thermal conductivity. Currently, molybdenum is widely used in stainless steel, machinery steel, and chemical products, and numerous studies aimed at investigating the use of molybdenum in high-value-added processes such as semiconductor manufacturing and liquid crystal display (LCD) sputtering are being conducted.1,2)

Normally, molybdenum metal is obtained from molybdenite as follows. Molybdenite is oxidation-roasted to obtain molybdenum trioxide, which is refined by heating to 1,273 K in air and subjected to sublimation refining or wet treatment, which involves the formation of ammonium molybdate. Refined molybdenum trioxide is converted into molybdenum metal by hydrogen reduction.3) Laboratory-scale reduction of molybdenum oxide and the relevant phase transition have been studied3–5) but there is no study aimed at determining the oxygen content of molybdenum metal or decreasing the oxygen content by optimizing the reduction conditions.

Recently, high-purity molybdenum, which contains very low amounts of metal and gas impurities, has been deemed necessary for LCD sputtering. The oxygen content of the commonly used 3N grade molybdenum powder is about 4,000 ppm, but the desired oxygen level for the sputtering target is known to be less than 100 ppm. The mechanical properties of molybdenum are very sensitive to the amounts of metal and gas impurities.6,7) Therefore, during the hydrogen reduction of molybdenum trioxide into molybdenum metal, it is necessary to optimize the reduction conditions and suppress the oxygen content. Vacuum arc melting (VAM) is a suitable method for decreasing the amounts of gas impurities; the equipment necessary for VAM is more economical compared to that for other melting processes, which makes it an affordable process.

In this study, we aimed to produce molybdenum ingots with low oxygen contents (<100 ppm) by optimizing the hydrogen reduction conditions and establishing the suitable conditions for oxygen content suppression via subsequent VAM process.

2. Experimental Procedure

The experimental procedure for this study is depicted in Fig. 1. 3N grade MoO₃ was used as the raw material. The experimental process involved two steps: hydrogen reduction and VAM. MoO₃ was reduced in a tubular furnace containing a quartz tube 50 mm in inner diameter and 1,000 mm in length. MoO₃ was placed at the center of a high-purity aluminum boat 120 mm in length and 20 mm in width. Both ends of the quartz tube were sealed using silicon, and an Ar + 5% H₂ mixture was injected from one end. At the opposite end of the quartz tube, the moisture content of the

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Fig. 1 Flow diagrams of the experimental procedure.
exhaust gas was measured using a thermohydrometer (KINMO KTH 350). The reaction temperature and time were varied during the experiment, and the relative humidity of the exhaust gas was measured while increasing the reaction temperature at the rate of 8 K/min, to measure the changes in reduction with temperature. 45 g samples of the reduced molybdenum powder were removed from the quartz tube and pressed into a φ25 mm steel compaction mold under 20 MPa pressure to form compacts. The prepared molybdenum compacts were heated into sintered bodies in a vacuum furnace for 1 h at 1,773 K and 1.5 × 10⁻³ Pa.

The small laboratory-scale vacuum furnace used for the VAM experiment was a hydrocooling double chamber, the lower end of which was fused to a hydrocooling copper mold (φ55 mm) to produce button-shaped ingots. The melting current was fixed at around 400 A, and a tungsten electrode was used. The molybdenum sintered body was mounted on the VAM equipment and vacuum-exhausted to about 0.67 Pa. Button-shaped ingots were melted every 2.5 min at a low Ar + 5% H₂ gas pressure of 7.6 × 10⁴ Pa, and 5, 10 and 20 min of melting time was used for ingot production. The crystal structure of the final reduced material was determined using X-ray diffraction (XRD), and the phase was observed by electron microscopy. The changes in the oxygen content of the reduced material and button-shaped ingots were analyzed using a LECO TCH-600 analyzer. Gas measurements were performed thrice on the button-shaped molybdenum ingots, and the average of the measurement results was used.

3. Results and Discussion

3.1 Molybdenum trioxide reduction

Since MoO₃ is known to sublime at around 973 K, the temperature during the reduction process has to be controlled accurately. In this study, we varied the temperature during MoO₃ hydrogen reduction to determine the optimal temperature for reduction; the results are listed in Table 1. Primary reduction was carried out by heating 10 g of MoO₃ at 823 and 873 K for 1 h under H₂/Ar (1:1) atmosphere (1.0 × 10⁻³ m³/min). The results showed that MoO₃ had sublimed locally, and pure MoO₂ could not be recovered. When the material was heated to 773 K under the same conditions, pure MoO₂ could be recovered. Secondary reduction was performed under normal metal production conditions, i.e., by heating MoO₂ at 1,273 K for 1 h while injecting a 1:1 mixture of H₂ and Ar gas (1.0 × 10⁻³ m³/min), and pure molybdenum was recovered. The current maximum recovered amount of MoO₂ in laboratory-scale experimentation, 30 g, was heated under the same conditions. In this case, the weight increased, and MoO₂ was not completely reduced to MoO₂, indicating that MoO₃ existed with the reduced molybdenum. To achieve complete reduction to MoO₂ in the primary reduction, we increased the heat treatment time to 2 h, but MoO₂ still remained after the secondary reduction.

Normally, H₂O produced during the reduction of MoO₃ must be removed by providing sufficient H₂ so that secondary oxidation is prevented. The amount of H₂ injected was varied using a mass flow controller (MFC) during hydrogen reduction in order to recover pure molybdenum. For every 1.0 × 10⁻³ m³/min of Ar gas, 1.0 × 10⁻³ and 2.0 × 10⁻³ m³/min of H₂ gas was injected during MoO₂ reduction. The XRD results for the recovered sample are shown in Fig. 2. As shown in the figure, when 1.0 × 10⁻³ m³/min of H₂ gas was injected, residual MoO₂ was present and pure molybdenum could not be recovered. This was probably because of the presence of secondary oxidation products resulting from the insufficient removal of the formed H₂O. When 2.0 × 10⁻³ m³/min of H₂ was injected during reduction, a pure molybdenum phase was formed. Our results showed that to obtain molybdenum metal by suppressing secondary oxidation, 2.0 × 10⁻³ m³/min of H₂ must be injected during hydrogen reduction so that oxidation by the H₂O produced during reduction is prevented.

We measured the level of H₂O during the reduction of MoO₃ after optimizing the reduction conditions through our experiments, using a hygrometer to measure the relative humidity. As shown in Fig. 3, the amount of H₂O within the tubular furnace decreased with heat treatment, between 0 and
773 K, and increased beyond 773 K. This phenomenon was thought to be because of the H\textsubscript{2}O produced during the hydrogen reduction of MoO\textsubscript{3} to MoO\textsubscript{2}. The reaction equation can be represented as shown in eq. (1). The H\textsubscript{2}O level decreased because of vaporization during the 2 h incubation at 773 K. However, secondary reduction between 773 and 1,273 K led to an increase in the amount of H\textsubscript{2}O. H\textsubscript{2}O was thought to be produced during the reduction of MoO\textsubscript{2} to molybdenum metal, as represented by eq. (2).\textsuperscript{8}

\[
\begin{align*}
\text{MoO}_3(s) + \text{H}_2(g) &= \text{MoO}_2(s) + \text{H}_2\text{O}(g) \\
\Delta G^0_{(1)} &= -74,775 - 28.685T (\text{J/mol}) \quad (1) \\
\frac{1}{2}\text{MoO}_2(s) + \text{H}_2(g) &= \frac{1}{2}\text{Mo}(s) + \text{H}_2\text{O}(g) \\
\Delta G^0_{(2)} &= 38,580 - 27.53T (\text{J/mol}) \quad (2)
\end{align*}
\]

Figure 4 shows the results of electron microscopy observations of the reduced material for various raw MoO\textsubscript{3} material and hydrogen contents. The MoO\textsubscript{3} particles formed in the early stages had sharp angles and were crystalline. At a H\textsubscript{2} injection rate of 1.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min, mostly fine particles were formed. It is well known that the molybdenum particle size differs depending on the relative humidity in the furnace during hydrogen reduction.\textsuperscript{3,4} When the H\textsubscript{2} injection rate was increased to 2.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min, the particles formed previously under the 1.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min conditions increased in size and became spherical. Similar to previous results, the relative furnace humidity was lower at 2.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min than at 1.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min. This influenced particle growth; the particles grew while maintaining the exterior phase owing to the tensile strength between the particle surfaces.\textsuperscript{4}

3.2 Oxygen impurities within molybdenum

Normally, the mechanical properties of molybdenum are very sensitive to the levels of metal and gas impurities.\textsuperscript{6,7} In this study, we measured the oxygen content of the ingots produced by the reduction of MoO\textsubscript{3} to molybdenum powder, degasification, and repeated VAM. Table 2 lists the oxygen content of the molybdenum powder obtained through the hydrogen reduction of MoO\textsubscript{3}. The oxygen content was 42,100 ppm when reduction was performed under 1.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min of H\textsubscript{2} and was much lower (4,930 ppm) when reduction was performed under 2.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min H\textsubscript{2}. The high oxygen content in the former case was thought to be due to the residual MoO\textsubscript{2} in the molybdenum metal, which in turn was because of the low H\textsubscript{2} level of 1.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min. Normally, thermal vacuum treatment is used for degassing during ingot production. At high temperatures and low pressures, removal of metal and gas impurities is possible because of the low vapor pressure.\textsuperscript{9,10} At 1.0 × 10\textsuperscript{-3} m\textsuperscript{3}/min
of H₂, the oxygen content of the reduced molybdenum was 34,400 ppm, which was about 8,000 ppm lower than that before degasification. At 2.0 \( \times 10^{-3} \) m³/min of H₂, the oxygen content of the reduced molybdenum was 3,040 ppm, which was 1,900 ppm lower than that before heat treatment. Because the oxygen level was high because of the residual MoO₂ when reduction was performed under 1.0 \( \times 10^{-3} \) m³/min H₂, the material was not suitable for VAM. In this study, we subjected the molybdenum metal reduced under 2.0 \( \times 10^{-3} \) m³/min of H₂ after degasification to repeated melting. The oxygen content tended to decrease from the initial value of 3,040 ppm after degasification by repeated VAM under Ar + 5%H₂. When the material was melted for 20 min, the oxygen content decreased further to 90 ppm, allowing for the production of a low-oxygen ingot appropriate for sputtering. This is thought to be because of the removal of H₂O by the increased H₂ level and the high vapor pressure of MoO₂.x11)

4. Conclusion

In this study, we successfully produced a low-oxygen (<100 ppm) molybdenum ingot by optimizing the hydrogen reduction conditions and subsequent VAM. We established the optimal conditions for hydrogen reduction and heat treatment appropriate for laboratory-scale experiments and measured the oxygen content and phase changes by varying the amount of H₂ injected. We could obtain pure molybdenum metal when 30 g of MoO₃ was reduced under 2.0 \( \times 10^{-3} \) m³/min of H₂ and 1.0 \( \times 10^{-3} \) m³/min of Ar for 2 h at 773 K as primary reduction, and for 1 h at 1,273 K as secondary reduction. The amount of oxygen, considered an impurity in molybdenum preparation, in the ingot reduced to 90 ppm during hydrogen reduction; this could be attributed to the refining effect, i.e., removal of H₂O by increasing the H₂ level, and the high vapor pressure of MoO₂. The molybdenum ingot with low oxygen content of less than 100 ppm has high economic potential as the raw material for sputtering targets.

Acknowledgement

This research was supported by the General Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Knowledge Economy of Korea.

REFERENCES


Table 2 Analytical results of oxygen impurities by hydrogen reduction and VAM.

<table>
<thead>
<tr>
<th>Reduction &amp; melting condition</th>
<th>After hydrogen reduction</th>
<th>After Heat treatment</th>
<th>After melting for 5 min</th>
<th>After melting for 10 min</th>
<th>After melting for 20 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo powder (H₂ 1.0 ( \times 10^{-3} ) m³/min, 30 g, 2 h)</td>
<td>42,100 ppm</td>
<td>34,400 ppm</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mo powder (H₂ 2.0 ( \times 10^{-3} ) m³/min, 30 g, 2 h)</td>
<td>4,930 ppm</td>
<td>3,000 ppm</td>
<td>1,170 ppm</td>
<td>540 ppm</td>
<td>90 ppm</td>
</tr>
</tbody>
</table>