Molybdenum Alloy "MSB Series" for Hot Extrusion Dies

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Extrusion tools made of refractory metals, such as molybdenum (Mo) and tungsten, are used in increasingly severe environments. Nevertheless, these tools are required to have superior mechanical properties, long life, and excellent reliability. We have developed a new Mo alloy "MSB" for hot extrusion dies used in plastic working, by using a dispersed Mo-base intermetallic compound. The MSB exhibited superior mechanical properties compared with conventional Mo alloys at temperatures below 1000°C. In addition, by adding a titanium alloy to the MSB, we have developed another alloy "T-MSB" that has high mechanical properties at high temperatures. In the hot extrusion of brass, dies made of these Mo alloys had 2.5 times longer tool life than conventional Mo dies.

Keywords: molybdenum, mechanical properties, hot extrusion die

1. Introduction

Molybdenum (Mo) is one of the high melting point metals. It is used in high heat load environments (e.g. as components for high temperature heating furnaces) by taking full advantage of its characteristics such as high melting point (2,630°C) and low vapor pressure.(1) In general, Mo powder is pressed and sintered, and final products of various shapes are manufactured by hot or cold plastic working and machining. Mo plastic working materials have superb mechanical properties. However, when recrystallized after being exposed to high temperature, their properties decrease significantly. TZM (Mo-0.5Ti-0.08Zr-C) alloy(2)-(4) is well known as a material with improved mechanical properties. It is manufactured by dissolving an appropriate amount of titanium (Ti) and zirconium (Zr) and dispersing carbide particles such as TiC and ZrC. The alloy has been used in various applications.

For example, TZM is used for dies for hot extrusion of billets (e.g. brass) heated at 700–900°C.(5) However, these dies cause problems during use, such as changes in hole dimensions (i.e. hole deformation) and cracks in dies. The deformation and cracks cause defective shapes, dimensions, or appearance of extruded materials. This poses issues in manufacturing extruded materials.

To solve these issues, the dies must ensure high strength and high toughness at the usage temperature. Yoshimi et al.(6) conducted research on ultra-high temperature materials such as turbine blades for jet engines used in severe environments. They proved that the Mo-Si-B alloy (an ingot material) derived from Mo_5SiB_2 (a hard material achieved by adding silicon (Si) and boron (B) to Mo, Vickers hardness: 1,600 HV) demonstrated extremely high strength at high temperature. The strength of the Mo-Si-B alloy at 900°C is very high, about 18 times that of the TZM alloy.

We found that the strength can be improved by adding only small amounts of Mo_5SiB_2 when the powder metallurgy process, in which A.L.M.T. Corp. has strength, is used. We developed the MSB series, Mo alloys that demonstrate high strength particularly in the temperature range in which dies are used. This paper reports the details of these efforts.

2. Manufacturing Method of MSB Series and Evaluation of Properties

Si-alloy and B-alloy powders were added and mixed with the Mo powder to synthesize the Mo_5SiB_2 powder by high temperature heat treatment. The Mo_5SiB_2 powder was milled for grain size control and used for developing the MSB series.

A specified amount of Mo_5SiB_2 powder was added and mixed with the Mo powder. Hydrogen sintering was performed after cold isostatic pressing.*1 The sintered material was subjected to hot plastic working to create a Mo processing material with Mo_5SiB_2 added. This material is referred to as "MSB." We prepared another material by adding the Ti-alloy powder in the mixing process. The material was created under the same conditions. This material is referred to as "T-MSB."

The MSB series was evaluated for strength by the tensile test and three-point bending test, hardness by the Vickers hardness test, and oxidation mass loss properties by heating in the atmosphere. For comparison in each evaluation, we used TZM and pure Mo whose plastic working rate was equivalent to that of MSB.

3. Results of Properties Evaluation of MSB Series

3-1 Tensile properties

To evaluate the tensile properties, we used test pieces that were 1 mm thick and 8 mm long in the parallel part. Test pieces were heated to different temperatures from room temperature (maximum temperature: 1,500°C), and evaluated at an initial strain rate of 6.7×10^{-4} s^{-1}. The results of the tensile test are shown in Fig. 1. MSB demonstrated strength exceeding that of the TZM alloy at 900°C or lower and 1,400°C or higher. We assume that the strength increased by adding Mo_5SiB_2, which is characterized by high hardness.

Meanwhile, the strength of MSB was slightly lower than that of TZM at 1,200°C. We investigated this phenomenon based on the changes in hardness of each material. Figure 2 shows the results of measurement of the Vickers hardness (load: 10 kgf, retention time: 15 sec) at room temperature after heat treatment of each material at the specified temperatures for one hour. The hardness of MSB was lower than that of TZM after heat treatment at 1,000°C and 1,200°C. We estimated the temperature at which recrystallization*2 started based on the hardness change: about 900°C for MSB and pure Mo, and about 1,100°C for TZM. The behavior of MSB was similar to that of pure Mo because Mo is the matrix.*3 For TZM, Ti and Zr are partially dissolved in the Mo matrix. Thus, the temperature at which recrystallization starts shifts to the high temperature side.[(7),(8)] Thus, the strength of MSB is considered to have been increased by adding Mo_5SiB_2. However, the difference in hardness due to recrystallization is considered to have affected the strength at around 1,200°C. At 1,400°C or higher, the hardness of TZM was lower than that of MSB due to increased recrystallization. Thus, the strength of MSB is considered to have been higher than that of TZM.

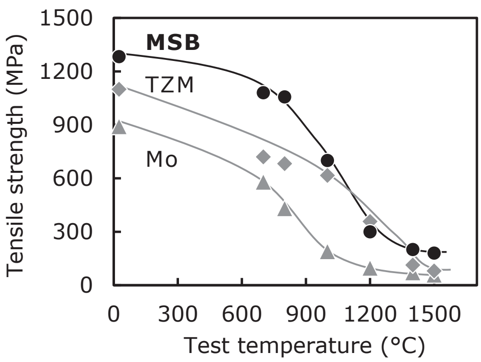

Fig. 1. Results of tensile test

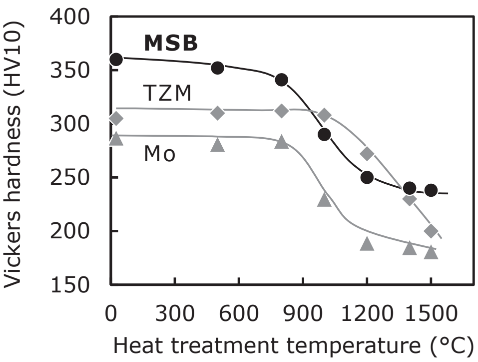

Fig. 2. Results of hardness measurement

3-2 Bending properties

To verify the bending properties, we used test pieces that were 1 mm thick, 3 mm wide, and 20 mm long. Both ends were supported, with an inter-fulcrum distance of 16 mm. The test pieces were heated at different temperatures (500–1200°C), and evaluated at an initial strain rate of 1.9 $\times 10^{-4}$ s^{-1} based on the three-point bending test. The results of the bending test are shown in Fig. 3. The strength of MSB was higher than that of TZM at 900°C or lower. The strength of T-MSB was higher than that of TZM at 1,200°C or lower (upper limit of the range in this test). At 800°C, which is the general extrusion temperature for copper alloys, the strength of MSB and T-MSB was about double and triple of that of the TZM alloy, respectively. Regarding the tensile properties (Fig. 1), the strength of MSB was lower than that of TZM at around 1,200°C. The strength of T-MSB (with a Ti alloy added) was high at all the temperatures. This is supposed to be attributable to dissolution and dispersion strengthening by the added Ti alloy. This requires further elucidation.

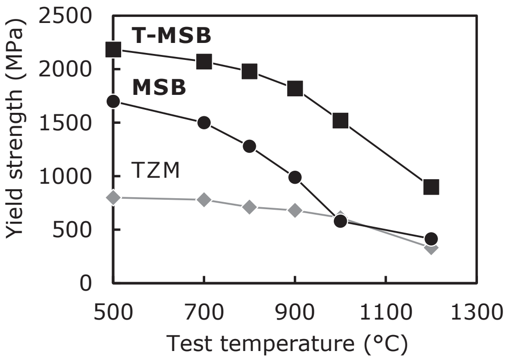

Fig. 3. Results of bending test

3-3 Hot hardness

To measure hot hardness, we used test pieces cut into cubes measuring 10 mm on each side. The test pieces were heated from room temperature to 1,000°C, and the Vickers hardness (load: 1 kgf, retention time: 15 sec) was measured at the specified temperatures. The measurement results are shown in Fig. 4. The hardness of MSB was almost equiva-

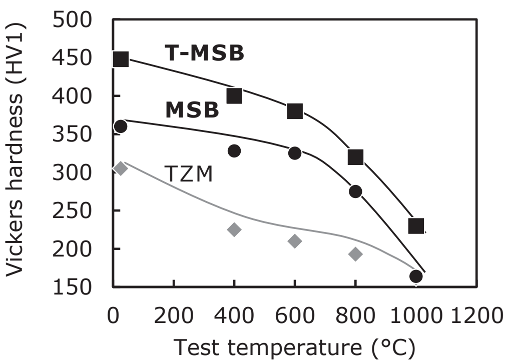

Fig. 4. Results of hot hardness measurement

lent to that of TZM at 1,000°C. However, the hardness of MSB was higher than that of TZM up to 1,000°C. The hardness of T-MSB, whose strength was higher than that of TZM in the three-point bending test, was higher than that of TZM at all the temperatures.

3-4 Oxidation mass loss properties

Mo starts to oxidize when the temperature exceeds 400°C. At 700°C or higher, MoO_3 is generated, and Mo is rapidly depleted.(1) Basically, extrusion of brass and other metals is performed in the atmosphere. To maintain the precision of the hole shape of a die, the die should use a material with low oxidation mass loss. Thus, a thermogravimetric analyzer*3 was used to evaluate the oxidation mass loss properties. Test pieces that were cut into cubes measuring 1 mm on each side were set on the balance in the equipment. Air was allowed to flow into the equipment at 25 mL/min. The test pieces were heated up to 1,100°C at the heating rate of 5°C/min to determine the changes in weight. Figure 5 shows the results. No significant change was observed for all the materials up to 800°C. The mass started to decrease when the temperature exceeded 800°C. However, the behavior was different between the MSB series and TZM/Mo. The decrease rate of the MSB series was low. The cross-sectional structure of MSB and TZM after the test is shown in Fig. 6.

On the surface of TZM, a thick layer of MoO_3 formed by oxidation was observed. Meanwhile, a Si-O-based oxide film was formed on the surface of MSB. Mo_5SiB_2 that was added served as the source supplying Si to form the Si-O-based oxide film. We assume that the oxide film suppressed the diffusion of oxygen into the matrix and decreased the oxidation mass loss rate.

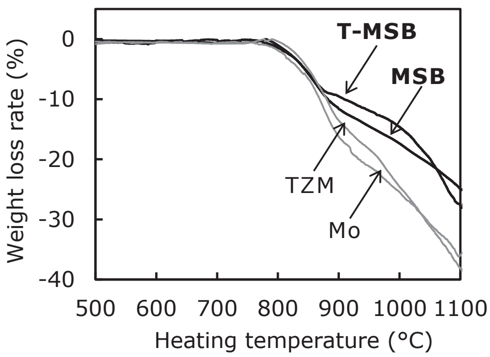

Fig. 5. Results of thermogravimetry

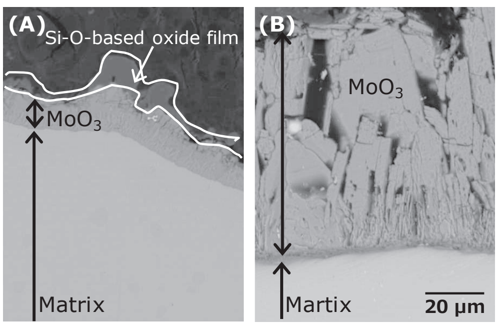

Fig. 6. Cross-sectional structure after thermogravimetry test

4. Evaluation as Hot Extrusion Die

Figure 7 shows a hot extrusion die and its image of usage. A T-MSB die was used to extrude brass at about 800°C. For the conventional Mo alloy die, the dimensional change from the target diameter reached about 1.5% or higher at about 800 extrusion cycles, and the die was no longer usable. For the T-MSB die, the dimensional change was 0.6% or lower at more than 2,000 extrusion cycles. The T-MSB die demonstrated excellent dimensional precision and service life 2.5 times or longer than that of the conventional Mo alloy die (Fig. 8).

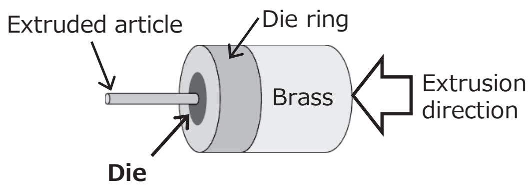

Fig. 7. Extrusion image

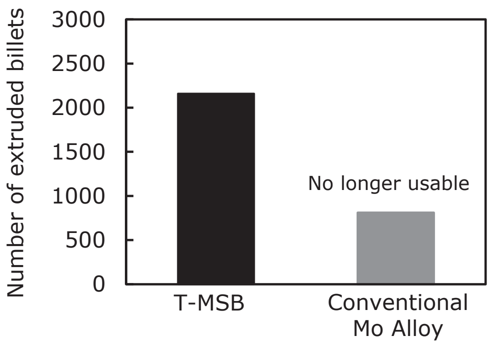

Fig. 8. Results of brass extrusion

5. Conclusion

To extend the service life of Mo alloy dies that are used for extrusion of brass and other metals, we developed MSB and T-MSB, which are new Mo alloys derived from powder metallurgy by using Mo_5SiB_2 characterized by high hardness.

These new alloys demonstrated high strength and hardness compared to TZM, an existing high-strength Mo material, at a temperature around 800°C (general extrusion temperature). They also demonstrated oxidation resistance.

A.L.M.T. Corp. started to sell the MSB series mainly for hot extrusion dies. At present, the company has been working to expand sales to deploy these alloys not only for plastic work tools but also for applications requiring superb heat resistance and wear resistance.

• MSB is a trademark or registered trademark of A.L.M.T. Corp.

Technical Terms

∗1 Cold isostatic pressing: A process of pressurizing powder into a solid state (powder pressurization). Liquid such as water is used as a pressure medium in applying isotropic pressure to a container in which powder is placed.

∗2 Recrystallization: A phenomenon in which new crystal grains (with significantly low dislocation density) are generated and grow due to energy accumulated in the material when a metallic material subjected to plastic working is retained at high temperature.

∗3 Matrix: A phase that makes up the majority of the volume of a material. It is also referred to as "parent phase."

∗4 Thermogravimetry: Defined as a method of measuring the mass of a specimen as a function of temperature while changing the specimen temperature based on a specific program. In this method, changes in the mass of a specimen are continuously measured when the specimen is heated or cooled. Thermogravimetry is used to evaluate changes in mass due to chemical changes such as oxidation and reduction.

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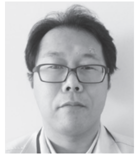

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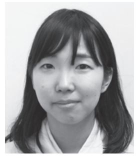

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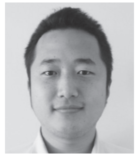

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