Addition of an Aminic Antioxidant to a Hindered Ester-Based Heat Resisting Oil to Improve Lubrication for Press Forming of Magnesium Alloy Sheets

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High heat resistance is required for the lubricant used during the mass production of press formed magnesium parts using a warm press forming process. The heat resistance of a hindered ester has previously been found to be high, but insufficient at temperatures around 573 K. Therefore, further improvement of hindered ester-based heat resisting lubricants is required. This paper describes the influence on lubricity of adding aminic antioxidants to hindered esters. The results showed that excellent heat resistance was obtained by adding 5 to 20% styrenated diphenylamine. While a 5% addition improved heat resistance and inhibited lubricant degradation, addition of 10 or 20% additive resulted in decreased lubricity. Furthermore, the best lubricity was obtained when DLC-coated carbide was used as the die material in combination with the lubricant containing aminic antioxidant. [doi:10.2320/matertrans.47.1782]

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1. Introduction

Magnesium is used to manufacture notebook computer cases, camera bodies, mobile phone bodies and automotive parts to reduce their weight. Casting processes such as diecasting and thixomolding have usually been used to produce magnesium products, although press forming of metal sheets is preferred to boost productivity. Magnesium alloys have a hexagonal close-packed structure and ductility increases at elevated temperatures as slippage on non-basal planes progressively improves. However, magnesium alloys have poor formability around room temperature because of recessive slippage on non-basal planes. These characteristics of magnesium can be accommodated by warm press forming.¹

In order to apply warm press forming to mass-production, an appropriate lubricant is required. If a mineral oil-based liquid lubricant is used, its low heat resistance may lead to scorching and detract from the desired product properties. By the same token, build up of scorch on metal dies decreases dimensional accuracy and causes cracking or denting of the magnesium products.

To prevent these defects, solid lubricants such as graphite or molybdenum disulfide are commonly used for warm press forming. However, the brittleness and high activity of magnesium alloy will complicate mass production by impeding the cleaning of such solid lubricants in post-production processes.

Therefore, hindered ester-based heat resistant lubricants have been evaluated for planned mass production of magnesium parts, where its higher heat resistance capacity compared to other types of liquid lubricants will be utilized. In deep drawing, dies should be heated to approximately 573 K. As a result, a greater heat resistance is required for the lubricant used. During an experiment conducted at approximately 573 K, a lubricant consisting of only hindered ester had insufficient heat resistance, which resulted in scorching.

The purpose of this research was to confirm improvement of heat resistance by adding an aminic antioxidant to a hindered ester type lubricant and to examine the effect of an aminic antioxidant on lubricity using a flat-die drawing test. In addition, a heat-resistant lubricant was applied to different die materials in a flat-die drawing test to determine the best die material for lubricity.

2. Test Methods

2.1 Sample oils

Pentaerythritol C7 to C10 saturated fatty acid ester and dipentaerythritol iso C9 fatty acid ester were mixed to make the base oil. Styrenated diphenylamine, an aminic antioxidant, was added to the base oil at seven concentrations to produce the sample oils. Kinematic viscosity of the sample oils was adjusted to 90–110 mm² s⁻¹ (at 313 K) by changing the component ratios of the two hindered esters. Table 1 shows the molecular structures of the chemical compounds constituting sample oils. Table 2 shows the compositions, kinematic viscosity and density of the blended sample oils.

2.2 Heat resistance test

A muffle furnace was utilized to run a heat resistance test using a steel cup. The sample oil (1 × 10⁻³ kg) was contained in the cup, which was heated to and held at 573 K for 2 hours in the furnace before measuring thermal degradation and volatilization of the oil. Some oils carbonized due to their poor heat resistance. After the test, the cups were rinsed by ultrasonic cleaning in n-hexane to measure the amount of persistent carbon residues scorched onto the cups. An oil of lower heat resistance produced more carbon residue due to excessive scorching, while an oil of the higher heat resistance produced less carbon residue because it apparently retards scorching. Similarly, the sample oils were tested to find the optimum concentration of styrenated diphenylamine for higher heat resistance.

2.3 Evaluation of lubricity using a flat-die drawing test

Sample oils that provided high heat resistance in the heat resistance test were used in a flat-die drawing test with a
magnesium-alloy sheet. Figure 1 is a schematic diagram of the drawing test. The test oil was applied at 2°C to the surface of an AZ31B sheet which was 0.8 mm thick, 50 mm wide and 250 mm long. Dies 65 mm wide and 15 mm long and with a 3 mm shoulder radius were set on top of and underneath the test sheet. The die material was carbide with a micro-grain size of up to 1.0 μm and coated with DLC (diamond-like carbon). Each die was fixed to the die holder. The die holders were fixed in parallel to the type frame of the tester and oil pressure was exerted vertically from the upper part. The test sheet was put between the dies under a pressure of 6.6 MPa at 1.1 × 10⁻² ms⁻¹ and was drawn unidirectionally at a constant velocity of 8.3 × 10⁻³ ms⁻¹. The lubricating ability of the sample oil was evaluated by the coefficient of friction, the ratio of the drawing force and the die load, obtained by measuring the amount of pullout resistance during the test. These lubricity tests were run at room temperature and at 553 K by heating the upper and lower die using a thermocouple. The flat-die drawing test evaluates the sliding capacity between the surface of the metal sheet and dies, but does not evaluates the plastic deformation of the sheet. This test can evaluate simply the difference in the lubricity of the oils. Different die materials for the flat-die drawing test were also used to study their influence on the coefficient of friction. The three types of dies used for the flat-die drawing test were TiC-coated SKD dies, non-coated carbide dies and DLC-coated carbide dies.

### Table 1 Molecular structures of chemical compounds constituting sample oils.

<table>
<thead>
<tr>
<th>Description of chemical compounds</th>
<th>Molecular structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrenated diphenylamine</td>
<td><img src="image1" alt="Molecular structure" /></td>
</tr>
<tr>
<td>Pentaerythritol-C7–C10 ester</td>
<td><img src="image2" alt="Molecular structure" /></td>
</tr>
<tr>
<td>Dipentaerythritol-isoC9 ester</td>
<td><img src="image3" alt="Molecular structure" /></td>
</tr>
</tbody>
</table>

### Table 2 Composition and kinematic viscosity of blended sample oils.

<table>
<thead>
<tr>
<th>Sample oils</th>
<th>Styrenated diphenylamine (mass%)</th>
<th>Pentaerythritol-C7–C10 ester (mass%)</th>
<th>Dipentaerythritol-isoC9 ester (mass%)</th>
<th>Kinematic viscosity (mm² s⁻¹, 313 K)</th>
<th>Density (g cm⁻³, 288 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>75</td>
<td>25</td>
<td>96</td>
<td>0.97</td>
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<tr>
<td>5%</td>
<td>5</td>
<td>75</td>
<td>20</td>
<td>90</td>
<td>0.97</td>
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<tr>
<td>10%</td>
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<td>70</td>
<td>20</td>
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<td>20</td>
<td>65</td>
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<tr>
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<td>65</td>
<td>5</td>
<td>101</td>
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<td>50</td>
<td>0</td>
<td>110</td>
<td>1.03</td>
</tr>
</tbody>
</table>

3. Test Results

3.1 Results of the heat resistance test

Figure 2 shows the results of the heat resistance tests of oils consisting of different amounts of styrenated diphenylamine. Scorch content is shown as the ratio of the amount of
sample oil after and before the test. With no addition, about 15% scorching persisted on the cup whereas 5% additive significantly decreased the residual carbon. Increasing the additive content to 10% and 20% similarly reduced the amount of scorching observed. When the additive content was further increased to 30% and 40%, the amount of scorching increased slightly. An extremely large amount of residual carbon was observed with 50% additive. Figure 3 shows typical samples after a heat resistance test. One is with no styrenated diphenylamine and the other contained 5% styrenated diphenylamine. The additive free cup (a) was covered by residual carbon. The other cup (b) showed no residual carbon on the bottom but some on the side wall.

3.2 Results of the flat-die drawing test
At room temperature there was a relatively high coefficient of friction of about 0.3 with little difference between the additive-containing oils (Fig. 4). At a higher temperature of 553 K, the coefficient of friction was generally lower than that at room temperature. The addition of 5% styrenated diphenylamine yielded the lowest coefficient of friction of 0.17. When the amount of styrenated diphenylamine was increased to 10% or 20%, the coefficient of friction increased.

3.3 Lubricity properties using different die materials
Figure 5 shows the kinematic coefficient of friction for the different die materials in the flat-die drawing test. All three die materials (TiC-coated SKD dies, non-coated carbide dies and DLC-coated carbide dies) yielded a relatively high coefficient of friction at room temperature. However, at 553 K, the coefficient of friction for both the TiC-coated SKD dies and the non-coated carbide dies were unable to be measured due to rupture of the test pieces caused by higher friction. In the flat-die drawing test using DLC-coated carbide dies, the sheet was not ruptured at 553 K.

A photograph of AZ31B sheets taken after the test at 553 K is shown in Fig. 6.

4. Discussion

4.1 Correlation of styrenated diphenylamine concentration and heat resistance
Styrenated diphenylamine is one of the aminic antioxidants which behave like phenolic antioxidant as a radical scavenger. These substances scavenge radicals generated by
the amputation or cleavage of a carbon chain by heat or light. They stop consecutive auto-oxidation reactions of the carbon chain.\textsuperscript{3} After reviewing other aminic antioxidants, we chose styrenated diphenylamine because it is easy to formulate and its good inhibition properties minimize thermal oxidation. Based on heat resistance tests of hindered ester-based oils containing styrenated diphenylamine, it was determined that a content of 5% or greater styrenated diphenylamine gave acceptable results. When the sample oils containing less than 5% additive were tested, more scorch was produced than with 5% additive. Alternatively, radical chain oxidation reactions may generate scorch. Hindered esters are considered to possess comparatively high heat resistance among all types of oils. A hindered ester does not contain hydrogen atoms in the $\beta$-position of the alcohol part of the chemical structure. Therefore, decomposition through a six-membered ring structure is unable to proceed by hydrogen bonding. As decomposition requires an activation energy of 50 kJ or higher, the decomposition temperature also becomes 40 K higher than that required for typical diesters. Furthermore, hydrogen atoms attached to the $\alpha$-carbon of the fatty acids are heat-sensitive and easily decomposed. Additional thermal stability can be obtained by using fatty acids that have a branched-chain at this position.\textsuperscript{3,4} The hindered ester consists of pentaerythritol which is one of the hindered alcohols and some branch-chained or linear-chained unsaturated fatty acids with a carbon number of 7 to 10. The above-formulated hindered esters could have much higher heat resistant properties compared to other typical diesters or triglycerides. Nonetheless, the hindered ester did not perform as well as expected under the severe condition of 573 K for 2 hours. Scorching occurred in the test using an antioxidant-free sample, which resulted in about 15% carbide remaining. When a styrenated diphenylamine was added to increase heat resistance, a 5% addition dramatically diminished the amount of scorch observed (see Fig. 2). Styrenated diphenylamine has been commonly used to prevent consecutive macromolecular radical decomposition when compounding macromolecules in plastics and rubber. The effective concentrations used are typically from 0.1 to 1%.\textsuperscript{5} However, when a small amount of additive such as 0.1% was formulated into a lubricant for the flat-die drawing test, the amount of additive was not enough to provide acceptable heat-resistance since the lubricant was exposed to the dies at temperatures at about 553 K. Under these conditions, sufficient heat resistance was not obtained until the concentration of styrenated diphenylamine in the formulated lubricant was 5% or greater. Additive concentrations of 10% and 20% gave very high heat resistance with almost no scorching. However, the amount of scorching gradually increased at additive concentrations of 30% or higher. The sample with an additive concentration of 50% generated even more scorch than the sample without any additive. Despite the fact that styrenated diphenylamine stops acceleration of degradation via a radical chain reaction, it is postulated that decomposition products were also a cause of the scorch that was generated by thermal degradation and decomposition of the antioxidant itself.

4.2 Correlation of styrenated diphenylamine concentration and lubricity

The slippage of magnesium is enhanced by heat and it consequently increased lubricity by enhancing the sliding action of the test piece. Among all the concentrations tested, the lowest coefficient of friction was obtained from the 5% sample that did well in the heat resistance test and also maintained the oil film during the drawing test.

However, a gradual increase in concentration to 10% and 20% resulted in higher coefficients of friction at 553 K. This fact may be connected with the deterioration of degreasing ability of the fluids as the amount of styrenated diphenylamine added increased. An experiment was conducted using magnesium sheets to study the variation in degreasing time with increasing amounts of additive (Fig. 7). Oils containing different amounts of styrenated diphenylamine were applied to the sheets and then dipped in an alkaline degreasing solution. The fastest degreasing time was obtained for the sample without any additive. The sample containing 5% styrenated diphenylamine required approximately 1.3 times more degreasing time than the additive-free sample. The 20% sample took 1.8 times more degreasing time. These tests suggest that styrenated diphenylamine may be more strongly adsorbed onto magnesium sheets than the hindered esters used as base oil. Hindereder esters confer lubricity by forming a relatively thick oil film on magnesium sheets due to their long molecular chains and vertical sequences while styrenated diphenylamine cannot form a thick oil film given its small,

Fig. 6 Figures of AZ31B sheets after the flat-die drawing test. (a) Ruptured (b) Well-slid.
4.3 Choice of die material for magnesium sheet processing

Tests were performed on three kinds of dies with different construction and coating materials to determine how they influenced the coefficient of friction. At room temperature, the non-coated carbide dies produced a slightly higher coefficient of friction than the TiC-coated SKD dies and the DLC-coated carbide dies, which had almost the same coefficient of friction. It was also observed following the test that the surface of the non-coated carbide dies and the TiC-coated SKD dies had a substantial amount of magnesium adhesion. Further, when the non-coated carbide dies and the TiC coated SKD dies were tested at 553 K, the lubricities obtained were poor enough to induce rupture. The reasons why only the DLC-coated carbide dies gave a successful pullout of the magnesium sheet at 553 K are believed to be due to the good anti-adhesion of DLC to soft metal materials and DLC’s low elastic modulus allowing absorption of the resisting force during the operation despite its high hardness.

In conjunction with the previously described tests, a preliminary investigation was performed to determine the carbide grain size (rough-grains, fine-grains, micro-grains) that would provide the best lubricant performance by measuring differences of surface roughness and dynamic hardness for each grain size. Three kinds of carbide dies treated with DLC were applied to the flat-die drawing test. The surface roughness Ra and the dynamic hardness of the DLC-coated carbide dies are shown in Table 3. Dynamic hardness is shown as a ratio of load and a square depth.

All dies made with the three different type grain sizes showed lower hardness than TiC-coated SKD dies. The micro-grained dies yielded the lowest surface roughness while the rough-grained ones resulted in the highest. The surface roughness of TiC-coated SKD dies was closer to that of the micro-grained dies. Lubricity tests were performed with the result that the rough-grained carbide dies with DLC produced a nominally lower coefficient of friction and less adhesion of magnesium than the other DLC-coated carbide grain sizes in the flat-die drawing test at 553 K (Fig. 8). When the surfaces of the dies are rougher, the oil retention is improved and press forming of magnesium sheets may be better.

However, the most suitable surface roughness to optimize lubricant performance cannot be precisely determined yet as it may depend on different DLC adhesions obtained with different carbide grain sizes.

5. Conclusions

Based on the results obtained from addition of styrenated diphenylamine to the hindered esters, the following conclusions can be drawn from this investigation:

(1) Addition of 5% or greater styrenated diphenylamine to hindered esters dramatically improved heat resistance of the lubricant. However at concentrations of 40% or more heat resistance was adversely affected.

(2) Addition of 5% styrenated diphenylamine gave good lubricity and produced the lowest coefficient of friction of all the concentrations tested in the flat-die drawing test.

(3) DLC-coated carbide dies produced the best lubricity when using different die materials in the flat-die drawing test.
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REFERENCES