Effects of Fixing Carbon Nanoparticle to AZ91D Magnesium Alloy Chip Surface on Thixomold Forming*

Yoshiaki Hashimoto¹, Makoto Hino², Yutaka Mitooka³, Koji Murakami³ and Teruto Kanadani⁴

¹Okayama Factory, STU Co., LTD., Soja 719-1102, Japan

²Faculty of Engineering, Hiroshima Institute of Technology, Hiroshima 731-5193, Japan

³Industrial Technology Center of Okayama Prefecture, Okayama 701-1296, Japan

⁴Faculty of Engineering, Okayama University of Science, Okayama 700-0005, Japan

Thixomolded magnesium products have been applied as an alternative for plastic moldings in body frames for electronic equipments. AZ91D magnesium alloy chips are ordinarily used for thixomolding process. The carbon nanoparticle was fixed in the magnesium chip surface in order to improve the castability of thixomolding process. The manufacture of magnesium-carbon alloy is not easy, because carbon does not have the wettability for magnesium. However, the magnesium alloy chips fixed carbon nanoparticles make it possible to produce the magnesium-carbon alloy by thixomolding process. Since the fluidity of the magnesium alloy chip with carbon nanoparticle was improved in comparison with the AZ91D magnesium alloy chip, thin thickness molding became possible. In addition, mechanical properties of the thixomolded magnesium alloy made of the magnesium alloy chips fixed carbon nanoparticle were also improved.
[\[doi:10.2320/matertrans.L-M2015839\]](https://doi.org/10.2320/matertrans.L-M2015839)

(Received November 4, 2015; Accepted November 24, 2015; Published January 25, 2016)

Keywords: AZ91D magnesium alloy, carbon nanoparticle, surface modification, thixomold forming

1. Introduction

Magnesium alloys have been applied as an alternative for plastic moldings in body frames for electronic equipment because of their light weight, high rigidity, good heat dissipation, high damping capacity, good electromagnetic shielding effectiveness, and good recycling ability.¹⁾ Both sheet metal thinning and complicated shapes are required for the body frames of electronic equipment made of magnesium alloys. At present, the thixomolding process has been widely applied to meet the performance requirements.²⁾

Reducing the weight and size of mobile electronic equipment such as smartphones and tablets is highly desirable and requires improvement of the mechanical properties and further thinning of the thixomolded magnesium frames. Thus far, the thixomolding process optimizes the molding conditions, including the injection speed, injection temperature, die temperature, and die improvements, to make it possible to form thin magnesium frames with complex shapes. However, further optimization of the molding conditions to improve the thinning and mechanical properties is difficult.

On the other hand, the grains become finer by adding carbon to the magnesium alloy, and these magnesium-carbon alloys make it possible to improve the mechanical properties.³⁾ However, it is extremely difficult to alloy carbon into magnesium because carbon does not have the required wettability for magnesium.

In the thixomolding process, magnesium-alloy ingots are shattered to produce metal chips, which are used as raw material. These chips are extruded through a heating cylinder by a screw, and magnesium alloy is then injected at high speed into the designed die. Finally, magnesium chips are molded into the final product form.⁴⁾ Therefore, the

manufacturing of magnesium-carbon alloys could become feasible if magnesium-alloy chips with carbon fixed to the surface can be used as a raw material in the thixomolding process.

In this study, we produced a new magnesium alloy that included carbon by using the conventional AZ91D magnesium-alloy chip fixed with carbon nanoparticles as the raw material for the thixomolding process. The effects of fixing carbon to the magnesium-alloy chip surface on the formability during the thixomolding process and the subsequent mechanical properties of the thixomolded specimen were further examined.

2. Experimental Procedure

Magnesium-alloy chips of approximately 4 mm in size were cut from a commercial AZ91D magnesium-alloy ingot using a chipping machine for subsequent use in the thixomolding process. Table 1 shows the chemical compositions of the AZ91D alloy chips. The chips were agitated in the presence of 0.1 mass% carbon nanoparticles using a mixer in order to induce the adherence of the carbon to the chip surface.

The thixomolding process was conducted with a magnesium thixomolding machine (JLM 280MG from Japan Steel Works Ltd.) under a clamping force of 2744 kN. The AZ91D magnesium-alloy chips with and without carbon nanoparticles were used in the thixomolding process and the thixomolded specimen was 200 mm in length, 100 mm in width, and 2 mm in thickness. The chemical composition of the thixomolded specimen was examined by emission spectrophotometric analysis (Shimadzu Corporation, PDA-7000). A smaller specimen was removed from the thixomolded block for subsequent tensile testing using an Instron 3382 Floor Model Universal Testing System following the JIS Z 2201 standard. The dimensions of the tensile test specimen were as follows: parallel body length-

*This Paper was Originally Published in Japanese in JILM 65 (2015) 118–122.

Table 1 Chemical composition of AZ91D magnesium alloy chip (mass%).

	Al	Zn	Mn	Si	Fe	Cu	Ni	Be	Other matallic	C	Mg
AZ91D chip	8.91	0.65	0.22	0.03	0.002	0.003	0.0008	0.001	<0.001	0.01	bal.

Fig. 1 Appearance of thixomolded specimen and drawing of tensile test specimen.

60 mm, width-10 mm, thickness-2 mm, gauge length-50 mm (Fig. 1).

The fluidity of the injection molding process is the most important property required to perform the sheet metal thinning and produce complicated shapes; thus the flowability was evaluated by measuring the flow length during a thixomolding process performed in a spiral-type die with a wall thickness of 0.5 mm. Internal defects caused by the thixomolding process, such as shrinkage cavities were examined by an X-ray computed tomography scanner (TOSCANER-32300μhd; Toshiba IT & Control Systems Corporation).

3. Results and Discussion

3.1 Magnesium-alloy chip fixed with carbon nanoparticles

Figure 2 shows the secondary electron image of the carbon nanoparticles. The average particle size was approximately 30 nm, and these particles appeared to have been cohered without dispersing. The nanoparticles were added to the chips produced from the AZ91D magnesium-alloy ingot (hereafter the AZ91D chip), and the carbon nanoparticles were then made to adhere onto the chip surface by agitation with a mixer (hereafter the carbon fixed chip). The appearances of the AZ91D chips and the carbon fixed chips are shown in Fig. 3. The AZ91D chips were a bright silver color, but carbon fixed chips were black. The change of appearance indicated that the carbon nanoparticles adhered to the AZ91D chip surface.

Figure 4 shows the secondary electron image of the carbon nanoparticles fixed to the chip surface. The loose carbon nanoparticles did not appear to uniformly adhere to the chip surface, while the cohered carbon nanoparticles partially adhered, as shown by the arrows. The terminal group of the carbon surface was modified by functional groups such as carboxyl, hydroxyl, and aldehyde groups in order to improve the bonding between the carbon nanoparticles and the magnesium-alloy chip surface.

Fig. 2 Secondary electron image of carbon nanoparticles.

Fig. 3 Appearances of the magnesium chips; (a) AZ91D chips, (b) Carbon fixed chips.

Fig. 4 Secondary electron image of carbon fixed chip.

Table 2 Chemical composition of thixomolded specimens made of AZ91D chip and Carbon fixed chip (mass%).

	Al	Zn	Mn	Si	Fe	Cu	Ni	Be	Other metallic	C	Mg
AZ91D chip	9.2	0.65	0.22	0.03	0.004	0.003	0.0007	0.0010	<0.001	0.01	bal.
Carbon fixed chip	9.1	0.66	0.21	0.03	0.003	0.003	0.0008	0.0007	<0.001	0.10	bal.

3.2 Effect of carbon fixed to the magnesium-alloy chip surface on the thixomolding process

3.2.1 Thixomolding process

The thixomold forming process was undertaken under the same conditions using either the AZ91D chip alone or the carbon fixed chip as a raw material. Table 2 shows the chemical composition of the thixomolded specimens made of the AZ91D chip and the carbon fixed chip. The chemical compositions of the AZ91D chip (Table 1) and the thixomolded one made from the AZ91D chip were similar. The chemical composition of the thixomolded specimen made from the carbon fixed chip was the same as that of the thixomolded one made from the AZ91D chip, with the exception of carbon. The carbon content of the thixomolded specimen made from the AZ91D chip was 0.1 mass%, and this value was similar to the carbon content added to the AZ91D chip to prepare the carbon fixed chips. This result indicated that the carbon nanoparticles fixed to the magnesium chip surface were almost completely incorporated into the specimen during the thixomolding process.

3.2.2 Flowability

The fluidity of the injection molding process is the most important property required to perform the sheet metal thinning and produce complicated shapes; thus the flowability was evaluated by measuring the flow length during a thixomolding process performed in a spiral-type die with a wall thickness of 0.5 mm. Figure 5 shows the appearances of the thixomolded specimens prepared from the AZ91D chips and carbon fixed chips under the same conditions (i.e., injection temperature: 853 K, injection speed: 2.5 m/s, $N=5$). The flow length of the carbon fixed chip was drastically improved compared to that of the AZ91D chip.

Figure 6 shows the appearance of the thixomolded specimen made from the carbon fixed chips. The product size was approximately $100 \times 50 \text{ mm}^2$. Difficulties were encountered when attempting to form molds using the 0.3-mm-thick AZ91D chips. In contrast, the molding process was feasible when using 0.28-mm-thick carbon fixed chips under the same conditions (Fig. 6). Based on these results, the modification of the AZ91D chip surface by carbon nanoparticles improved the flowability, and thus enabled molding of thin walls, which was difficult when using the chips without carbon modification.

The effect on the flowability by the carbon nanoparticles fixed to the magnesium chip surface was considered as follows. Graphite with a six-membered ring structure is often used as a solid lubricant, and thus, carbon nanoparticles with the same six-membered ring structure likely have the same lubricating effect. Therefore, the carbon nanoparticles fixed to the chip surface could have caused a reduction in the friction coefficients of the chip as well as of the region between the metallic interior and the chip in the cylinder to improve fluidity. However, this lubricating effect appeared to

be lost in the injection molding process into the metal die, because most of the magnesium-alloy chips melted and thus caused the carbon nanoparticles fixed to the chip surface to become stirred. The small 0.1 mass% carbon content in the molten metal improved fluidity, as shown in this study, though it is unlikely that the melting point and eutectic point drastically changed by this minute amount of carbon in the magnesium alloy. The carbon nanoparticles may have affected the fluidity between the metal die and the molten metal surface because of the lubricating effect of the nanoparticles. However, since the parting compounds were applied to the metal die surface for the purpose of improving the fluidity, another factor that was not related to the lubricating effect appeared to exist, which resulted in the improved fluidity of the molten metal. In the future, more detailed examinations on this point will be carried out.

3.2.3 Internal defect in the thixomolded specimen

The thixomolding process using the AZ91D chip has been widely applied for parts with thin walls and complicated shapes, whereas the production of parts with wall thicknesses of greater than a millimeter is highly desired for the thixomolding process. However, internal defects such as blow holes tend to occur with the increase in the wall thickness of the thixomolded part, and these internal defects have prevented the wide application of the process for objects such as automobile parts.

To test this, the thixomold forming process was undertaken by a dumbbell-shaped metal die for subsequent tensile testing (parallel body diameter: 10 mm) using the AZ91D chip and carbon fixed chip under the same conditions. Figure 7 shows the appearances of the specimens with the dumbbell shape and the 3D image of the internal defects using an X-ray computed tomography scanner. The measurement was performed at the parallel body of each specimen in the area denoted by the broken line (Fig. 7). A number of internal defects were observed with the thixomolded specimen made from the AZ91D chip; however, the number of internal defects in the specimen made from the carbon fixed chip was drastically reduced. These results showed that the carbon modification to the chip surface was quite useful for controlling the internal defects in the thick part of the thixomolding process. The reduction in the number of internal defects by carbon nanoparticle modification was closely related to the improvement in flowability, which was presumed to be based on promoting the filling of the molten metal into the metal die inside. However, the actual reason for this is currently unknown, and further examination is needed.

3.2.4 Tensile properties

Figure 8 shows the stress-strain chart from the tensile tests of the thixomolded specimens made of the AZ91D chip and carbon fixed chip. The modulus of longitudinal elasticity of

Fig. 5 Appearances of fluidity testing by thixomolding; (a) AZ91D chip, (b) Carbon fixed chip.

Fig. 6 Appearance of thixomolded specimen (100 mm × 50 mm) made of carbon fixed chip.

Fig. 8 Stress-strain chart for thixomolded specimens.

Fig. 7 Observation results of thixomolded specimens using X-ray CT scanner; (a) AZ91D chip, (b) Carbon fixed chip.

the specimens from both AZ91D chip and carbon fixed chip in the elastic region was the same; however, the 0.2% proof stress, tensile strength, and elongation were observed to be improved by the carbon addition. The mean values of tensile properties ($N = 5$) are shown in Table 3.

These results revealed that the small amount of carbon in the AZ91D magnesium alloy produced by the thixomolding process contributed to the improvement in the tensile

Table 3 Mechanical properties of thixomolded specimens made of AZ91D chip and Carbon fixed chip.

	0.2% proof stress (MPa)	Tensile strength (MPa)	Elongation (%)
AZ91D chip	158	186	2.0
Carbon fixed chip	187	213	3.0

properties. Thus far, the manufacture of magnesium–carbon alloys has been difficult because carbon does not have the required wettability for magnesium. However, the magnesium–alloy chips fixed with carbon nanoparticles made it possible to produce a magnesium–carbon alloy using the thixomolding process. In addition, the application of the carbon fixed chip enabled improvements in the castability and the tensile properties.⁵⁾

4. Conclusion

In this study, we produced a new magnesium–carbon alloy by using the conventional AZ91D magnesium–alloy chip fixed with carbon nanoparticles as the raw material for the thixomolding process. Furthermore, the effects of carbon fixed to the magnesium–alloy chip surface on the formability for the thixomolding process and the tensile properties of the thixomolded specimen were examined.

- (1) The carbon nanoparticles could be successfully fixed to the surface of the magnesium chips after the addition of 0.1 mass% of carbon nanoparticles to the chips with subsequent agitation by a mixer.
- (2) Since the thixomolded specimen produced by 0.1 mass% carbon fixed chips contained 0.1 mass% carbon, most of the carbon was assumed to be fixed to the chip surface. Therefore, it was possible to produce the carbon addition to the magnesium alloy by this process without much difficulty.

- (3) The carbon nanoparticles fixed to the chip surface appeared to improve the castability, including the improvement in the flowability and suppression, and this was attributed to the nanoparticles acting as a solid lubricant. The tensile properties of the thixomolded specimen were also improved by the use of the carbon fixed chip.

Acknowledgment

Authors would like to express sincere thanks to the Small and Medium Enterprise Agency, the Ministry of Economy, Trade and Industry, Japan for providing the Research Grant-in-Aid for the promotion of this research, and to Japan Steel Works Ltd.

REFERENCES

- 1) Y. Kojima: *J. Jpn. Inst. Light Met.* **58** (2008) 526–548 (in Japanese).
- 2) M. Hino, M. Hiramatsu, K. Murakami, A. Saijo and T. Kanadani: *J. Jpn. Inst. Light Met.* **56** (2006) 386–392 (in Japanese).
- 3) M. Makino, T. Kawata and H. Hane: *J. Jpn. Inst. Light Met.* **42** (1992) 810–814 (in Japanese).
- 4) T. Toshima: *Magunesiumu-Gokin no Kibangizyutsu to Oyotenkai*, (CMC Publishing CO., LTD., 2012) pp. 35–44 (in Japanese).
- 5) Y. Mitooka, M. Hino, K. Murakami, H. Uchiyama and Y. Hashimoto: Japan patent 5137049, China patent ZL201280002710.7, Republic of Korea patent 10-1310622.