Features and Vehicle Application of Heat Resistant Die Cast Magnesium Alloy

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Since the successful development of the world's first AZ91 alloy sheet, which has high strength and superior corrosion resistance, we started the magnesium alloy business with the AZ91 alloy sheet used for the case body of mobile electronic devices. For application to transportation vehicle parts, however, the properties of AZ91 were not sufficient and we launched the development of new Mg alloys. Recently we have successfully developed a high-temperature creep resistant Mg alloy that can be applied to automobile powertrain components through a collaborative research with the University of Toyama. The new alloy has overcome the drawbacks of conventional creep resistant Mg alloys, such as the low castability and inferior recyclability. This paper introduces major properties of the developed alloys, which are necessary for practical applications in transportation vehicle parts.

Keywords: creep-resistant, heat-resistant, magnesium alloy, die casting, weight reduction

1. Introduction

Magnesium (Mg) is the lightest of all practical structural metals. Its specific gravity is 1.8, or 2/3 that of aluminum (Al) and 1/4 that of iron (Fe). Alloys of magnesium that contain various added elements have been developed for specific purposes. Typical magnesium alloys include highly corrosion resistant AZ91D*[1] and high strength AM60 and AM50.*[2] In the automotive sector, these alloys are used to form the cores of steering wheels and ignition locks to take advantage of their high specific strength and rigidity.[(1)] These products are almost castings due to the low workability of magnesium alloys. Die casting*[3] is the method used to manufacture them because the technique is suitable for mass production and is relatively effective for rapid cooling.[(1)]

The use of a magnesium alloy is expected to achieve a substantial weight reduction of some parts, notably heavy power train components such as the oil pan and transmission case. While these components are required to be heat resistant, the heat resistance of AZ91 and AM60 is poor. At a temperature of 150°C, these alloys develop creep deformation, resulting in loosening of the fastening bolts. This issue makes AZ91 and AM60 unsuitable for power train components.[(2)] The heat resistance of AZ91 and AM60 is low because β-phase precipitates ($Mg_{17}Al_{12}$) noticeably decrease in strength at 120°C and higher temperatures, although their strength is high at room temperature.[(3)] As a solution to this challenge, the addition of aluminum is reduced to limit the precipitation of the β-phase and silicon (Si), rare-earth elements (REs), calcium (Ca), and strontium (Sr) are added individually or in combination to form precipitates that are stable at high temperatures. Thus heat-resistant magnesium alloys have been developed and put into practical use. However, some challenges needed to be overcome with these alloys, such as poor castability and recycling difficulties.[(2)] Sumitomo Electric Industries, Ltd., jointly with the University of Toyama, has recently successfully developed a heat-resistant magnesium alloy, overcoming problems associated with the use of heat-resistant magnesium alloys.

2. Development of Heat-Resistant Magnesium Alloys

2-1 Effects of added elements and design of existing alloys

Added elements in magnesium used to improve the alloy's heat resistance have been considered to exert the following effects.[(1),(3)]

Aluminum, if added to a high level, forms precipitates of the β-phase (Mg-Al compound symbolized as $Mg_{17}Al_{12}$), which reduces the strength of the alloy at high temperatures, resulting in the alloy's declining heat-resistant characteristics. However, it is an element the addition of which to some extent is considered to be indispensable for improved castability, corrosion resistance, and room temperature strength. In general, approximately 9% of Aluminum contained in the alloy is regarded effective in terms of castability, corrosion resistance, and room temperature strength. However, to ensure heat resistance, the selected level is 6% or less in many cases, compromising the above-mentioned characteristics. Rare earths (Res) improve the alloy's heat resistance by forming Al-RE precipitates of high-temperature strength. However, REs are highly active and therefore readily form stable oxides, reacting with oxygen in the atmosphere. When recycling an alloy containing an RE, it is necessary to use an expensive, special, purpose-prepared flux designed for RE-added alloys.

Silicon improves the alloy's heat resistance by forming fine particles of an intermetallic Mg-Si compound of improved high-temperature strength at grain boundaries. Nevertheless, compared with REs, the heat resistance improvement effect of silicon is small.

Calcium improves the alloy's heat resistance by forming an Al-Ca compound of improved high-temperature strength. However, the addition of a large amount of calcium forms a thick layer of oxide on the surface of molten metal. The inclusion of the oxide in a casting results in a material defect.

Strontium is also effective in improving the alloy's heat resistance by forming an Al-Sr compound of improved high-temperature strength. However, strontium is generally thought to reduce the alloy's castability. Table 1 summarizes the features of the above-described elements. A challenge facing existing heat-resistant alloys was that their castability, corrosion resistance, and recyclability were compromised to some degree although heat resistance was provided by reducing the percentage of aluminum and adding suitable amounts of calcium, strontium, and REs.[(2),(3)]

Table 1. Effects of added elements on characteristics

Element	Heat-resistant characteristics	Castability	Material strength	Corrosion resistance	Recyclability
Al	↓↓	↑	↑↑	↑	↑↑
RE	↑↑	↓	↑	↑	↓↓
Si	↑	↑	↑	−	−
Sr	↑	↓	↑	−	↓
Ca	↑↑	↓↓	↑	−	↓

↑: Improved ↓: Reduced −: Minor effect

2-2 Designing alloy compositions

To address the above-mentioned conventional challenges, Sumitomo Electric has worked on the development of alloys with improved castability, corrosion resistance, and recyclability as well as improved heat resistance. One prerequisite was to use aluminum at approximately 9% to ensure the alloy's castability, corrosion resistance, and recyclability. The goal was to reduce the amount of problematic β-phase precipitates or, ultimately, to inhibit precipitation. For this reason, we searched for elements that would allow aluminum to form a compound prior to magnesium and provide heat resistance. Possible candidate elements were REs, calcium, and strontium. The addition of an RE makes recycling difficult. Also, calcium, if added at a percentage of 2% or more, will make recycling difficult due to an increasing amount of oxides. Consequently, our idea was to use a combination of strontium and a small amount of calcium to limit β-phase precipitates. Since strontium forms compounds such as Al_2Sr and Al_4Sr and calcium forms an Al_2Ca compound, we explored the percentages of strontium and calcium required to reduce the percentage of aluminum to a level that would not form the β-phase. The results of the exploration showed that using strontium and calcium at 3% and 1%, respectively, would prevent the β-phase from forming even if the percentage of aluminum was 9%. As with general magnesium alloys, a trace amount of manganese (Mn) was used as an added element to reduce iron contained as an impurity by capturing it into Al-Mn compounds.[(4)] The constituent elements of the newly developed heat-resistant magnesium alloy (hereinafter referred to as "AJX931") are magnesium, aluminum, and strontium. These are also constituent elements of casting aluminum alloys. Therefore, the newly developed alloy is expected to be reused as an alloying material for aluminum alloys.

2-3 Evaluation of characteristics of newly developed alloy and existing alloys

Of the existing heat-resistant magnesium alloys, AS31 (Mg-Al-Si alloy), AE44 (Mg-Al-RE alloy), and MRI153M (Mg-Al-Ca-Sr alloy) are currently used in mass-produced vehicles. These three alloys[(2),(6)] were compared with AJX931 and evaluated. Table 2 presents the chemical compositions of the evaluated alloys.

Evaluation samples were prepared by a cold chamber die-casting machine with a die clamping force of 650 t. Figure 1 shows the exterior of the prepared sample. The sample was shaped to allow for the evaluation of castability, heat resistance, and mechanical characteristics. All samples used for the evaluation, including those used for comparison purposes, were die-cast into the illustrated shape.

Table 2. Chemical compositions of evaluated alloys

(mass%)

Alloy code	Al	Ca	Sr	RE	Si	Mn	Fe	Be	Mg
AS31	3.7	−	−	−	0.9	0.26	0.0008	0.0009	Bal.
MRI153M	7.7	1.0	0.25	−	−	0.23	0.0011	0.0026	Bal.
AE44	3.9	−	−	4.0	−	0.27	0.0006	0.0015	Bal.
AJX931	9.0	1.0	3.1	−	−	0.23	0.0014	−	Bal.

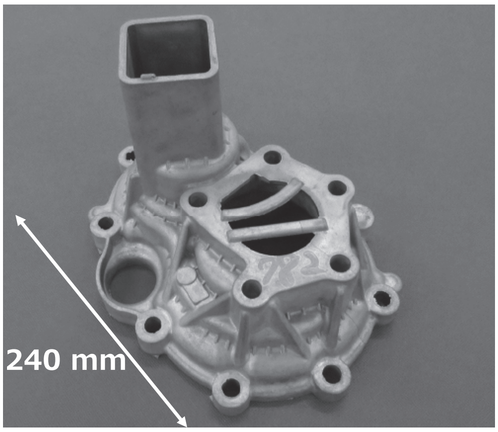

Fig. 1. Die-cast sample shape

3. Innovative Heat-Resistant Magnesium Alloy

3-1 Metallic structure of newly developed alloy

Figure 2 presents a cross-sectional image of the structure of an AJX931 die-cast sample, taken during scanning electron microscope (SEM) observation. The image reveals α-Mg primary phase in the black portions. Also shown are white precipitates and lamellar eutectic structures observed at voids between the cells and on grain boundaries. Figure 3 presents the metallic structure observed by field emission (FE)-SEM and the results of an analysis by energy-dispersive X-ray spectroscopy (EDX). Figure 4 shows X-ray diffraction (XRD) measurement results. According to these results, the compounds indicated in white in Fig. 3 are Al_2Sr and Al_4Sr, while those indicated in gray are C15-Al_2Ca or C36-$(Mg,Al)_2Ca$. Since die casting involves rapid cooling, it is highly likely that C36-$(Mg,Al)_2Ca$ dominantly precipitated. SEM observations showed no β-phase, proving that the exhibited structural form represented dominant precipita-

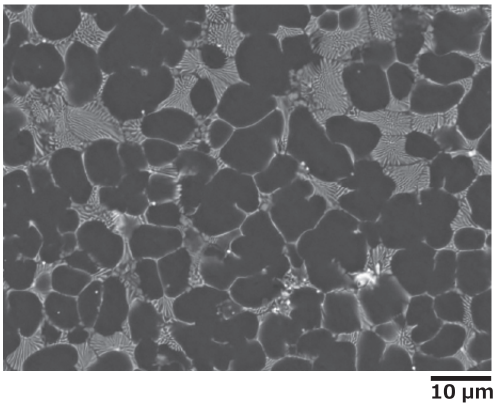

Fig. 2. Microstructure of AJX931 die casting

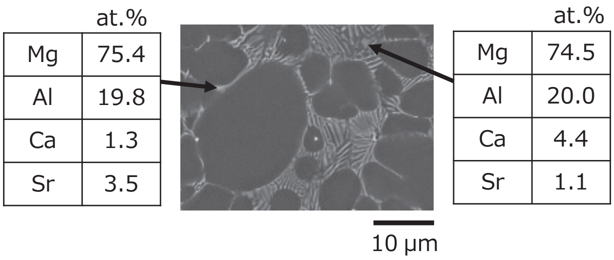

Fig. 3. FE-SEM-based EDX analysis of AJX931 die casting

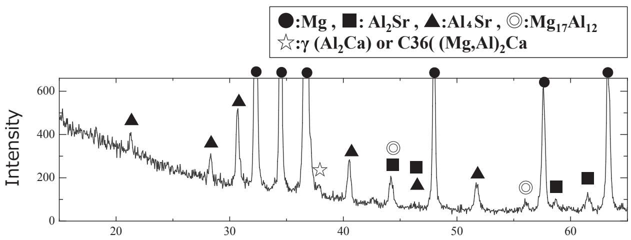

Fig. 4. XRD measurement of AJX931 die casting

tion of heat-resistant Al-Sr and Al-Ca compounds, as intended by the alloy design.

3-2 Heat-resistant characteristics

The alloy's heat-resistant characteristics were examined assuming an actual operating environment. M10 iron bolts were inserted through the boss holes 11 mm in diameter in the bottom of a casting, together with anodized aluminum washers intended to prevent galvanic corrosion, and attached to an aluminum alloy (ADC12) block, using an initial axial force of 13.5 kN. The casting was placed in a thermostatic chamber at 150°C for 300 h and then cooled to room temperature. Subsequently, decreases in tightening axial force were measured with the strain gage method (Fig. 5). Figure 6 presents the measurement results. The results have been arranged to show the ratio of remaining axial force to the initial tightening axial force (bolt-load retention: BLR). Higher remaining BLR implies higher heat resistance of the alloy. AZ91, measured for reference, exhibited a remaining BLR rate of 3%. AS31 and MRI153M are higher in heat resistance than AZ91, with their remaining BLR rates reaching between 28% and 36%. Nonetheless, these rates are only 30% to 50% of those of aluminum alloys that reach 80% to 90%. Therefore, replacing aluminum component materials with magnesium materials is thought to be impractical unless a substantial engineering change is made. Meanwhile, AJX931 and AE44 are higher in heat-resistant characteristics than other alloys, reaching 60%, which is 70% to 80% of aluminum alloys. They are expected to serve as material substitutes for aluminum alloys, requiring relatively minor engineering change. Despite its low RE and calcium contents, AJX931 compares favorably with, or surpasses, AE44 in heat resistance.

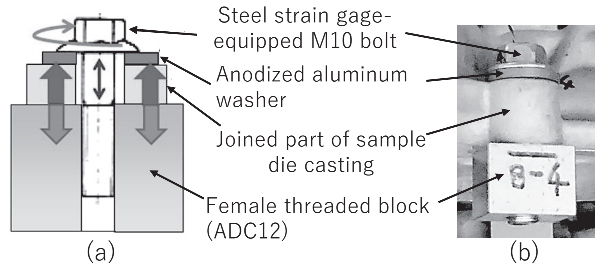

Fig. 5. Measurement method for remaining axial force

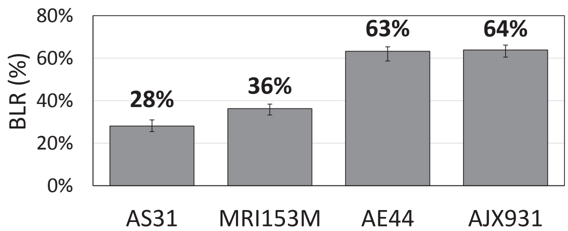

Fig. 6. BLR of conventional heat-resistant alloys and newly developed alloy

3-3 Castability for die casting (evaluation of casting cracks)

Figure 7 gives the crack evaluation results for the die castings. For the crack evaluation results, cracks were rated in proportion to the degree of cracking, ratings were counted for cracks developing in 10 castings, and the average crack rating per casting was presented as the casting-crack resistance of alloys. Points were assigned to cracks, as follows: 3 points if the opening was 0.5 mm wide or more, 2 points if the opening was streak-like and less than 0.5 mm wide and 10 mm long or more, and 1 point if smaller than above. With the shape shown in Fig. 1, AS31 scored 6.7 points and MRI153M, 11.5 points, in contrast to 2.0 points for AJX 931, which was a favorable result, although poorer than 0.3 points for AE44. Figure 8 shows the metallic structures of these alloys. Compared in structural form with crack-prone AS31 and MRI153M, less crack-prone AE44 and AJX931 had a larger amount of eutectic precipitates. Consequently, it can be inferred that, compared with AS31 and MRI153M, AJX931 and AE44 exhibited better feedability against solidification contraction and developed fewer cracks due to their structures closer to multi-eutectic composition.[5] Meanwhile, AJX931, which contains aluminum at 9% mass, is lower in melting point than other heat-resistant magnesium alloys by 30°C to 40°C. To melt magnesium, an iron crucible is generally used. When magnesium melts at 700°C or higher, iron leaches from the crucible into the molten metal, degrading the corrosion resistance of the metal. Therefore, magnesium is melted at less than 700°C. Heat-resistant magnesium alloys are melted typically at approximately 690°C with temperature variation taken into account. In that case, however, an alloy with a melting point of 620°C, for example, is provided with a degree of superheat*4 of only 70°C at the maximum. With AJX931, the degree of superheat can be set to 100°C to 110°C at the maximum, allowing the alloy to exhibit favorable fluidity due additionally to a larger amount of precipitation.

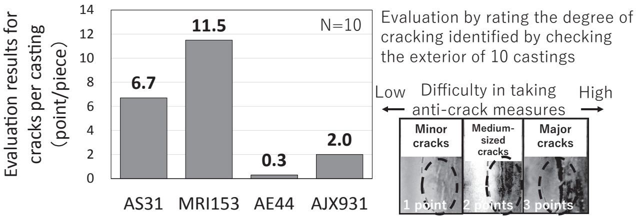

Fig. 7. Evaluation of castability for die casting (casting cracks)

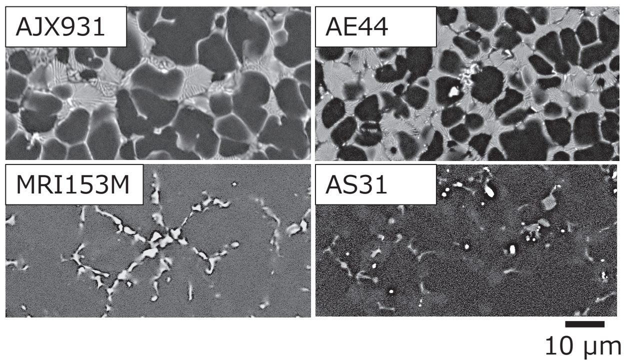

Fig. 8. Microstructures of die-cast alloys

3-4 Mechanical properties

The alloy's mechanical properties were evaluated by cutting out tensile test specimens in the shape illustrated in Fig. 9 from the predetermined flat area of the chimney-like portion of the sample shown in Fig. 1. Figure 10 gives the results of 0.2% yield strength required for designing components. The 0.2% yield strength of AS31 and AE44 is low because these alloys contain aluminum at 4% mass or less with the aim of improving their heat-resistant characteristics. In contrast, alloys that contain aluminum at 8% mass or more exhibited high 0.2% yield strength. Specifically, the newly developed alloy AJX931 exhibited the highest value of 156 MPa.

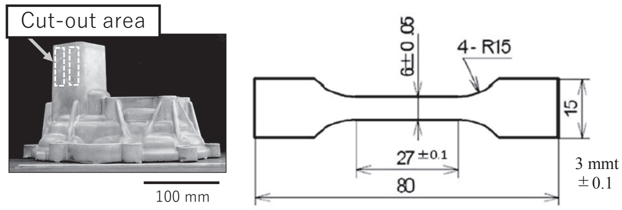

Fig. 9. Test specimen cut-out area and shape of tensile test specimen

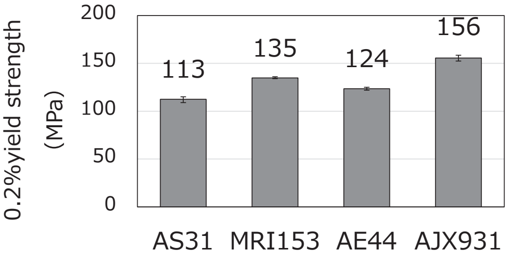

Fig. 10. 0.2% yield strength comparison of existing heat-resistant alloys and newly developed alloy

3-5 Corrosion-resistant characteristics

AJX931 and AE44, which are favorable in castability, were evaluated as to corrosion resistance.

Bare die-cast samples provided with no surface treatment or other similar process were subjected to 200 h salt spray testing (JIS Z 2371: 5% NaCl, 35°C). Figure 11 shows the exterior of the samples. Both alloys formed slight white rust. AE44 developed more pitting corrosion than AJX931 in areas that tended to collect water. In Fig. 11, the portions indicated with a box in the overall views, for example, are enlarged in the lower photos. The photos reveal that AJX931 is more resistant to corrosion than AE44 and its corrosion resistance is at a practical level.

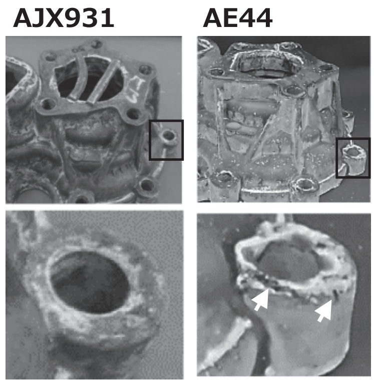

Fig. 11. Exterior of samples subjected to 200 h salt spray testing

3-6 Basic recyclability evaluation

We conducted a simple experiment to evaluate alloys as to their recyclability. A 50 kg original ingot was melted and 50 kg of die-casting scrap*5 was added into the melted ingot. After melting and smelting, the metal was cast into an ingot. Its recyclability was evaluated by examining impurities and inclusions, which are recycling concerns. During smelting, an iron pipe was used to blow argon gas into the molten metal. Commercially available AE44 contains approximately 15 ppm beryllium (Be) added to inhibit oxidation in the state of molten metal. Since beryllium decreases during re-melting, the experiment used Al-2.5%Be when melting the scrap, aiming at 20 ppm beryllium. Meanwhile, with AJX931, beryllium was not added because of the addition of calcium, which has a combustion prevention effect. Inclusions were evaluated, as follows: when melting the original ingot, when placing the scrap, and after smelting, the molten metal was sampled and cast into a bar; and inclusions present on a forced fracture surface were counted using a 10X magnifying glass. The alloys exhibited no major change in the main molten metal components between when melting the original ingot and when melting the scrap. While iron is an impurity that is most likely to be mixed during recycling, the concentration of iron in AJX931 after smelting was 24 ppm. One probable reason for this is the addition of a trace amount of manganese, which was effective for controlling iron at 50 ppm or below. Figure 12 gives evaluation results for inclusion levels. AE44 exhibited a slightly lower amount of inclusions in the molten state of the ingot. However, the amount of inclusions in AJX931 was lower both after the addition of the scrap and after smelting. Based on this finding, it is expected that AJX931 allows for easier removal of inclusions during recycling.

Figure 13 presents the exterior of ingots cast after smelting of AJX931 and AE44. Casting of both ingots was attempted in the atmosphere without blowing a shielding gas. However, AE44 showed discoloration and resulted in combustion. Therefore, AE44 was cast while blowing a shielding gas. Notwithstanding casting in the atmosphere, the ingot made of AJX931 had a white silver metallic sheen. In contrast, the surfaces of AE44 turned brown and showed combustion marks despite the addition of beryllium and blowing of a shielding gas. With AJX931, it is easier to maintain the molten metal clean and 1% mass calcium is effective in preventing combustion. Consequently, AJX931 proved itself to be easier to handle in molten state. However, dross*6 forming on the furnace walls was prone to combustion. Therefore, it was difficult to melt AJX931 fully without the use of a shielding gas.

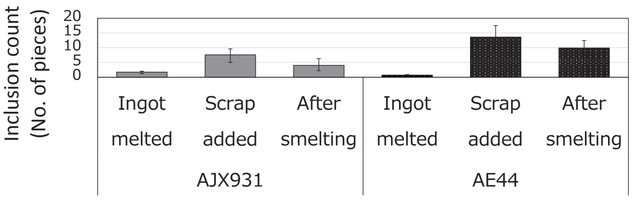

Fig. 12. Evaluation results for amount of inclusions

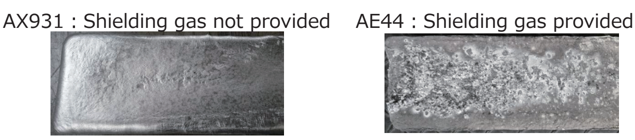

Fig. 13. Exterior of ingots cast from smelted molten metal

3-7 Overall evaluation

Heat-resistant magnesium alloys were evaluated as to their heat-resistant characteristics, castability (cracks), material strength (0.2% yield strength), corrosion resistance, and recyclability. In addition to AJX931, AE44 containing REs were favorable in terms of heat-resistant characteristics and castability, while AJX931 outperformed the other alloys in 0.2% yield strength, corrosion resistance, and recyclability.

4. Conclusion

Sumitomo Electric has successfully developed an innovative heat-resistant magnesium alloy, AJX931. Compared with existing heat-resistant magnesium alloys, AJX931 has highly heat-resistant characteristics, excellent castability, corrosion resistance, and material strength. Moreover, the newly developed alloy contains no RE as a constituent element and is therefore considered to facilitate recycling. We view AJX931 as a solution to concerns about conventional heat-resistant magnesium alloys. Expectations rest on this alloy for use in transportation vehicle parts. Future tasks include exploring its applications, aiming to practically use the newly developed alloy in vehicles.

Technical Terms

*1 AZ alloys: An alloy system of magnesium containing added aluminum and zinc with favorable strength and other mechanical properties.

*2 AM alloys: An alloy system of magnesium containing added aluminum with favorable tenacity.

*3 Die casting: A casting method that uses a high pressure to force molten metal into a precision mold for rapid solidification. This production process is frequently used to build automotive components due to the excellent surface texture and dimensional accuracy of the casting and high productivity.

*4 Degree of superheat: The difference between the temperature of a molten alloy and the alloy's melting point. Use of a high degree of superheat ensures fluidity of the molten metal during casting against temperature decreases, if any.

*5 Scrap: Scrap is necessarily produced by die casting, at the runner and riser where molten metal flows to the product cavity in the mold. After casting, these parts are removed from the product. It is desirable to recycle scrap from an environmental perspective as well as from the perspective of material cost.

*6 Dross: Oxides floating on the surface of molten metal.

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