Highly SCC Resistant 7000-series Aluminum Alloy Extrusion

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A study was conducted to develop extrusions of highstrength 7000-series aluminum alloy with excellent stress corrosion cracking (SCC) resistance. The target proof stress was 400MPa. Normally, the SCC resistance of 7000-series alloys decreases with increasing strength. This study focused on the mechanism of SCC; namely, the anodic dissolution of a boundary precipitate, MgZn₂. The electric potential of this precipitate was controlled to suppress its anodic dissolution and to improve the SCC resistance. In addition, the addition of Zr was confirmed to suppress recrystallization, and the surface recrystallization, which deteriorates SCC resistance, has been suppressed. This paper introduces the elemental technologies regarding the development of this alloy for achieving both high strength at the level. of 400 MPa proof stress and SCC resistance.

Introduction

Against the backdrop of recent environmental issues, strict fuel economy standards have been established for automobiles in Japan, North America, Europe, and other countries.¹⁾ Automobile manufacturers are promoting the weight reduction of vehicle bodies to improve fuel economy. One method of reducing vehicle body weight is to replace parts made of conventional low-strength iron with those made of high-tensile-strength steel or aluminum alloys having higher specific strength. The automobile parts that can be replaced with ones made of aluminum include bumpers, which are energy absorbing members for protecting occupants upon collision. In Japan, the use of aluminum for bumpers started in the 1990's, during which time the 6000-series alloys with a proof stress of 230MPa class were adapted, and 7000-series alloys with proof stress exceeding 300 MPa have partially been used since then. In recent years, further weight reduction needs and heightened collision-safety standards are expanding the demand for 7000-series alloys with a proof stress of 400MPa class.

In the case of 7000-series alloys, which are Al-Zn-Mg based, the sensitivity to stress corrosion cracking (hereinafter referred to as "SCC") increases with increasing strength.²⁾ The alloy newly developed this time focuses on the balance between the two contradicting characteristics of strength and SCC resistance. **Table 1** shows the mechanical properties (typical values) of an extrusion made of the new

Table1	Mechanical	properties	of	new	alloy	extrusion
	(Typical)					

Alloy	Temper	Yield Stress (MPa)	Tensile Strength (MPa)	Elongation (%)
New alloy	T7	400	450	14
7003	T5	255	315	15
7N01	T5	290	345	15

alloy. The strength is in the class of proof stress 400 MPa, which is more than 100 MPa higher than the strength of the typical 7000-series alloys conventionally used for welded structures. This paper introduces the method of improving SCC resistance, which was a point of development for the new alloy.

1. Occurrence mechanism of stress corrosion cracking

1.1 Theory for anodic dissolution of grain boundary precipitates

Fig. 1 is a schematic diagram showing the mechanism of SCC. Stress corrosion cracking of aluminum alloy is a phenomenon in which a crack occurs at a grain boundary and propagates from there when an alloy with a high SCC sensitivity is exposed to a corrosion environment under tensile stress exceeding a critical stress. Several theories exist for the mechanism of its occurrence, including a hydrogen embrittlement theory and mechanochemical theory.³⁾ During the development of the present alloy, attention was paid to the so-



Fig. 1 Schematic of SCC mechanism

called anodic dissolution theory,⁴⁾ which attributes the phenomenon to the dissolution of precipitates (MgZn₂ in the case of 7000-series alloys) on grain boundaries. To illustrate the anodic dissolution theory, a schematic diagram depicting the potential difference near the grain boundary is shown in Fig. 2. It is believed that the regions without precipitates, i.e. precipitate free zones (PFZs), have an electric potential higher than the potential inside grains due to the depletion of the solid solution elements, Zn and Mg. On the other hand, grain boundaries are dotted with precipitates (MgZn₂) sized larger than the intragranular precipitates. These grain boundary precipitates have the lowest electric potential, causing a significant potential difference with the PFZs. Once such a material is placed in a corrosive environment, the resulting potential difference causes the preferential dissolution of the grain boundary precipitates. In the development of the present alloy, the potential difference between PFZs and grain boundary precipitates was minimized to suppress the anodic dissolution of grain boundary precipitates and thus to improve SCC resistance. The method of minimizing the potential difference between PFZs and grain boundary precipitates will be described later.

1.2 Observation of SCC crack tip

The tip of an SCC crack that had occurred in a 7000-series alloy was observed in detail by SEM to elucidate the dissolution of MgZn₂ caused by anodic reaction. **Fig. 3** shows the SEM images of the SCC crack tip. The tested material was a T5-heat-treated material of a 7000-series alloy extruded for conventional bumpers. A specimen 2mm thick x 10mm wide x 50mm long was cut out from the extruded material in a direction vertical to the extrusion direction, and stress was applied using a three-point bending jig. In the SCC test, the specimen was immersed in a solution containing chromic acid (0.3%NaCl-3.0%K₂Cr₂O₇-3.6%CrO₃), which had been heated to a range from 95 to 100°C.



Fig. 2 Schematic of potential difference at grain boundary



Fig. 3 SEM images of SCC crack tip (Conventional 7000-series alloy)

The specimen surface was visually observed every 2 hours, and the test was interrupted upon SCC occurrence. The specimen was then subjected to SEM observation.

As shown in Fig. 3(c), $MgZn_2$ of about 100 to 200nm is observed on grain boundaries. Cavities, presumably caused by the melting of $MgZn_2$, were observed near the crack tip. These cavities on grain boundaries, caused by anodic dissolution of $MgZn_2$, were considered to be connected and propagated by the tensile stress applied to the crack tip.

2. Improvement of SCC resistance for developed alloy

2.1 Potential difference control at grain boundaries by Cu addition

It has been known that the addition of an element with noble potential, such as Ag and Cu, to 7000-series alloys improves their SCC resistance.⁵⁾ This is because the coexistence of Ag or Cu with MgZn₂ on grain boundaries reduces the difference in potential with PFZ and suppresses the anodic dissolution of MgZn₂. In the present alloy, Cu was selected because it is commonly used in many aluminum alloys and relatively inexpensive compared with Ag. Fig. 4 shows the effect of Cu addition on the SCC life of alloys. Three types of materials were tested: they all are in the form of extruded billet based on a 7000-series alloy and respectively contain 0%, 0.2% and 0.35% of Cu (the % expressions herein used represent weight percent). A hot-extrusion of a hollow rectangular pipe with a wall thickness of 2mm was subjected to artificial aging treatment. Specimens were cut out in the direction vertical to the extrusion direction. A three-point bending jig was used to apply stress,



and immersion test was conducted in chromic acid to compare SCC life. Increasing addition of Cu was found to increase the SCC life. Comparing at an applied stress that is 50% of the proof stress, SCC occurred after 12 hours in the material with no Cu addition, whereas no SCC occurred in the material with a 0.35% Cu addition. The addition of 0.35% of Cu improved SCC life by at least 30% compared with the material without additives.

Fig. 5 shows the EDX analysis results of grain boundary precipitates, $MgZn_2$, in the extrusions of the alloy with a Cu addition of 0.15% and 0.30% respectively. A trace amount of Cu was detected from the $MgZn_2$ on grain boundaries. The material with 0.30% Cu addition exhibits a peak that is twice higher than that of the material with 0.15% Cu addition. This indicates that the Cu content in MgZn₂ on grain boundaries tends to increase with the increasing addition of Cu. This effect is considered to have improved the SCC resistance.

2.2 Suppression of surface recrystallization

SCC is also affected by the size of grains. In 7000-series alloys, transition elements such as Mn, Cr and Zr are added to realize the pinning of grain boundaries by the precipitates of these elements. Extruded materials exhibit fibrous structures (partially with subgrains), in which grains are elongated in the direction of extrusion. On the other hand, extrusion surfaces are subjected to strong shear deformation due to friction between the dead metal and extruding die as they pass through the die. The resulting strain, along with processing heat and the heat of friction with the die, becomes the driving force to promote surface recrystallization. If the recrystallized grain generated in the extrusion surface layer is coarse, the SCC resistance is lowered. Hence, in the developed alloy, Zr was also added to suppress the surface recrystallization at the same time. Fig. 6 shows the relationship between the amount of Zr added to the base alloy and the suppression of recrystallization in the extruded material. When the Zr content is 0.08%, partially recrystallized grains are observed, indicating insufficient suppression of recrystallization. When



Fig. 5 EDX analysis of MgZn₂ on grain boundary of Cu-added alloys







(a) 0.12% Zr (conventional alloy)(b) 0.14% Zr (new alloy)Fig. 7 Micro structure of bumper surface made of new alloy

the Zr content is 0.14%, a fibrous structure is observed without any recrystallized grain. When the additive amount is at the maximum of 0.22%, the grain boundaries become even narrower and finer. When the additive amount of Zr exceeds 0.2%, there is a concern that the coarse primary crystals of ZrAl₃ may occur.⁶ Hence, the additive amount of 0.2% at the maximum is considered to be appropriate. Since the microstructure control is influenced by the extrusion ratio, the optimization study was conducted on an actual bumper extrusion.

Fig. 7 shows the optical micrographs of recrystallization on the surface of a bumper made of the new alloy. The figure compares the surface recrystallization layer of a conventional 7000-series alloy with that of the new alloy, wherein both the alloys have been extruded into the same cross section. In the newly developed alloy, the additive amount of Zr is at the minimum of 0.14%. The conventional alloy has a surface recrystallization layer with a thickness of about 300μ m. On the other hand, surface recrystallization was hardly observed when Zr was added in the amount of 0.14%. It has been confirmed that coarse surface recrystallization can be suppressed by adding 0.14% or more Zr even in the case of the material extruded to the actual bumper cross section. The practical development has been carried out on the new alloy for bumpers (proof stress 400MPa) by incorporating the elemental

technologies described above.

Conclusions

This paper has introduced elemental technologies for improving SCC resistance, the technologies adapted in the development of a new high-strength 7000-series alloy with excellent SCC resistance. Currently, the technology for the new alloy, 7K55, with a proof stress of 400MPa class has been established. There are plans to apply this alloy in the mass production of bumpers. In the future, the bar of technology development will be even raised, since even greater strength and improved SCC resistance will be required simultaneously. Hence, we focus on these element technologies and will continue to develop excellent alloys.

References

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