Rare Metal Materials and Engineering
Volume 47, Issue 6, June 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(6): 1739-1743.

ARTICLE

Effect of Ca Impurity on Microstructures and Mechanical Properties of As-Cast Al-5Mg Filler Alloy

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Abstract: Effects of Ca impurity on microstructures and mechanical properties of Al-5Mg filler alloys were investigated with SEM, EDS, XRD, tensile test and impact test. The results indicate that the phase composition of Al-5Mg alloy is affected by the Ca impurity. It is observed that block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ phase is distributed discontinuously along the grain boundaries when the content of Ca is less than 0.28 wt%. When the content of Ca is over 0.28 wt%, bar-like Al_2Ca and block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ combine together and are distributed along the grain boundaries, and the amount and size of Ca-rich phase (both the bar-like and block-like) increase with the increasing of Ca content. Tensile strength of the Al-5Mg alloys increases firstly and then decreases with the increasing Ca content, and the tensile strength gets to a maximum value when the content of Ca is 0.28 wt%. The plasticity and fracture toughness decrease slowly (Ca content 0 wt%~0.28 wt%) but then significantly decrease (Ca content>0.28 wt%), and the tensile or impact fracture mode transform from the transgranular ductile fracture to brittle cleavage fracture.

Key words: Al-5Mg filler alloy; Ca content; microstructures; mechanical properties

Fe, Si, Ga and Na, K are common impurities in the 5xxx and 7xxx aluminum alloys and exist in the form of eutectic compounds or brittle phase such as $AlFe_3$, $\alpha(FeSi_3Al_{12})$, $\beta(Fe_2Si_2Al_9)$, Al_7Cu_2Fe, $Al_6(FeMnSi)$ and Mg_2Si, which are hard to dissolve during heat treatment and are hazardous for aluminum alloys[1-3]. The Fe and Si-contained compounds distributed along the grain-boundaries cause plastic mismatching within the matrix and induce microcracks between grains, which weakens the fracture toughness of the alloys[4-6]. Detached Na atoms in Al-Mg alloys tend to concentrate along the grain boundaries and the interface of dendrite crystals, leading to the alloy cracking during heat treatment[7]. D. P. Mondal et al[8] reported effect of Ca addition on microstructure and compressive deformation behaviour of 7178 aluminum alloy. L. Huang et al[9] examined the effects of Ca on mechanical properties of cellular Al-Cu foams. However, the reports on the effects of Ca on microstructure and mechanical properties of Al-5Mg filler alloys are lacking.

The impurities of weld zone are from base materials and filler metals. Aluminum alloy welding wire is a common filler metal, which is usually manufactured after casting, extrusion and drawing process. Wire may be contaminated in the manufacture process and the Ca content increases. For instance, CaF_2 for smelting can remain in the melt. Besides, wire may be contaminated by dust or debris during extrusion, drawing, storage and so on. It is found that the mechanical properties of welded joint deteriorate because of Ca element. The microstructure of welded joint has an important effect on welding joint properties. Then welding metallurgy process and solidification structure is greatly influenced by the filler metals. Therefore, this study seeks to research the effect of Ca on microstructure and mechanical properties of Al-5Mg-0.1Mn-0.1Cr-0.1Ti alloys.

1 Experiment

In the experiment, 6 kinds of Al-5Mg-0.1Mn-0.1Cr-0.1Ti

Received date: June 23, 2017
Foundation item: International S&T Cooperation Program of China (2015DFA50470); Opening Project of National Engineering Research Center of Near-Net-Shape Forming for Metallic Materials (2013001)
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based alloys with Ca contents of 0.00 wt%~0.86 wt% were prepared. The Ca element was added in the form of Al-10%Ca master alloy. The smelting of alloys was conducted in an electric resistance furnace in a clay-graphite crucible. The temperature of alloy melt was kept between 720 and 750 °C. Castings were prepared by pouring liquid alloy into preheated cast iron molds of cylindrical shapes of 100 mm in length and 50 mm in diameter. The Ca content of alloys obtained by ICP-AWS (Inductively Coupled Plasma Atomic Emission Spectrometer) analysis is given in Table 1.

For microstructural characterization, the samples were cut from the ingot and polished using a standard metallographic technique. The samples were etched with Keller's reagent. Microstructure of the alloys was examined by scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS). Phase of the alloys was identified by Ultima Ⅳ X-ray diffraction (XRD). Tensile test was carried out using the MTS E45.105 test machine, with a cross-beam speed of 0.05 mm/s. Impact test was carried out by the Charpy pendulum impact test method. The size of the impact sample was 10 mm×10 mm×55 mm.

2 Results and Discussion

2.1 Effects of Ca on microstructure of alloys

Fig.1 shows the microstructures of the cast alloys with different contents of Ca. Although the matrix grains of six specimens are all refined equiaxed grains with the size of 60~80 μm, the precipitations along the grain boundaries are remarkably different. As shown in Fig.1a, the Al-5Mg-0.1Mn-0.1Cr-0.1Ti alloy without Ca has a microstructure of α-Al matrix and β-Al_3Mg_2 as the second phase, which is along the grain boundaries. By adding 0.05 wt% Ca, very fine (10 μm) Ca-rich massive phase appears at the grain boundaries of α-Al grains (Fig.1b). As the content of Ca increases from 0.12 wt% (Fig.1c) to 0.28 wt% (Fig.1d), the size of the Ca-rich phase keeps at a level of 10~30 μm but the number increases, and a new bar-like Ca-rich phase appears at the grain boundaries of the α-Al matrix. These new phases grow in size and amount with growth in Ca content until Ca content reaches 0.86 wt%. Fig.1f shows a new irregular polygon shaped massive phase and also aggregated bar-like phase. As a conclusion, when the content of Ca is less than 0.28 wt%, the Ca-rich phase are in the form of fine blocks; when the Ca content exceeds 0.28 wt%, bar-like phase begins to form along the grain boundaries of the matrix. The amount and size of the Ca-rich phase (both the bar-like and block-like) increase with increasing Ca content.

Table 1 Content of Ca in Al-5Mg-0.1Mn-0.1Cr-0.1Ti alloys (wt%)

Sample No.	1	2	3	4	5	6
Ca	-	0.05	0.12	0.28	0.51	0.86

Fig.2 shows the BSE image and EDS analysis results of the grain boundaries of the specimen with Ca content of 0.86 wt%. Fig.3 shows the XRD pattern of the alloy (0.86 wt% Ca). Combining Fig.1f and Fig.3, it can be found that the matrix of specimen (0.86 wt% Ca) is α-Al solution with Mg, and the precipitations along the grain boundaries are β-Al_3Mg_2 and Ca-rich phase. From Fig.2 two types of Ca-rich phase are

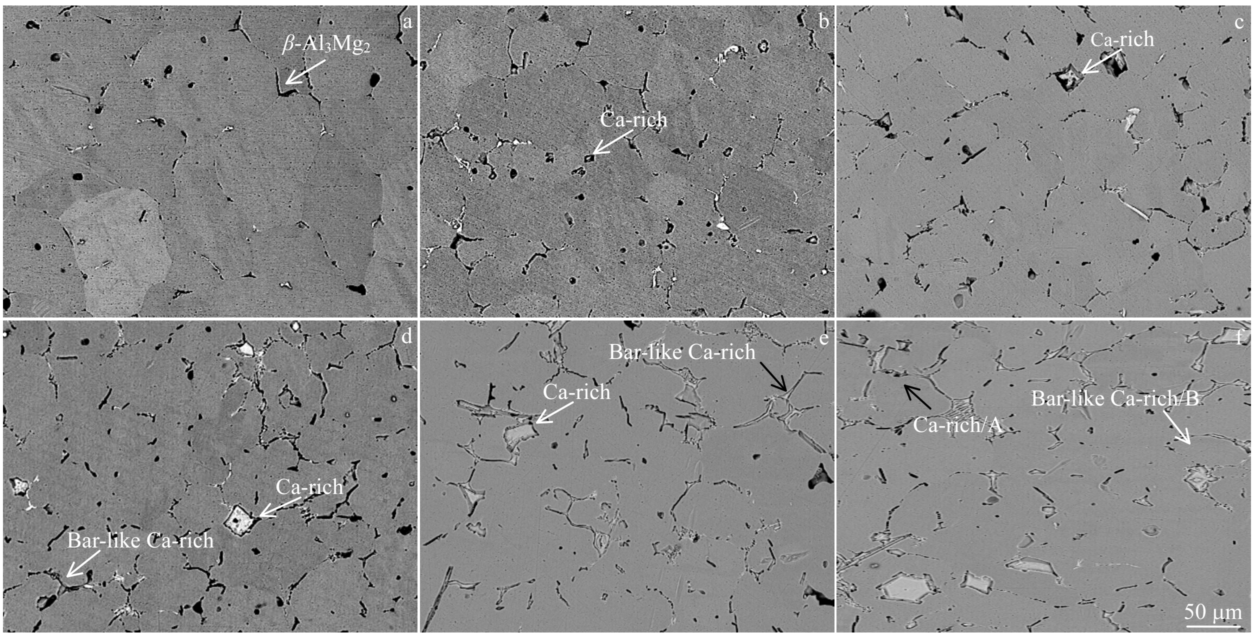

Fig.1 BSE micrographs of as-cast Al-Mg-Mn-Cr-Ti alloys with different Ca contents: (a) 0 wt% Ca, (b) 0.05 wt% Ca, (c) 0.12 wt% Ca, (d) 0.28 wt% Ca, (e) 0.51 wt% Ca, and (f) 0.86 wt% Ca

observed, discontinuous distributed bar-like phase and block-like phase. The block-like phase has a multilayer structure. The EDS analysis result shows that this phase contains Al, Mg, Ca, Cr and Ti, and the Al and Mg are matrix elements. The XRD analysis shows that the block-like phase could be $(Ti,Cr)_2Ca(Al,Mg)_{20}$. During equilibrium solidification, the content of Ca in Al can be up to 0.3 wt%. During non-equilibrium solidification, Ca in Al forms solid solution as well as compounds which are stable at room temperature.

Al_2Ca phase, Al_3Mg_2 phase and *α*-Al phase exist in Al-Mg-Ca alloys. As the standard enthalpy of formation of Al-Ca is lower than that of both Mg-Ca and Mg-Al, when Ca is added into the Al-Mg alloys, Al and Ca combine at the first place owing to a larger affinity[10,11]. Thus a thermodynamic stable intermetallic compound (IMC) Al_2Ca is formed. As Al_2Ca IMC grains grow much slower than that of the solid solution[12], its melting point (1079 °C) is much higher than that of *α*-Al. It is safe to predicate that the Al_2Ca is formed during initial solidification. As the sample metals used in experiment are Al, Mg, Ca, Cr and Ti, bar-like Al_2Ca and complex block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ IMC are formed in the final alloy.

The Al_2Ca IMC has an $MgCu_2$ structure-AB_2 laves structure. Since the Al_2Ca has a much larger lattice constant (*a*=0.8039 nm) than the *α*-Al matrix (*a*=0.405 nm), it could not use the former as the nucleation substrate. Al_2Ca grains are detached and pushed to matrix grain boundaries, where the concentration

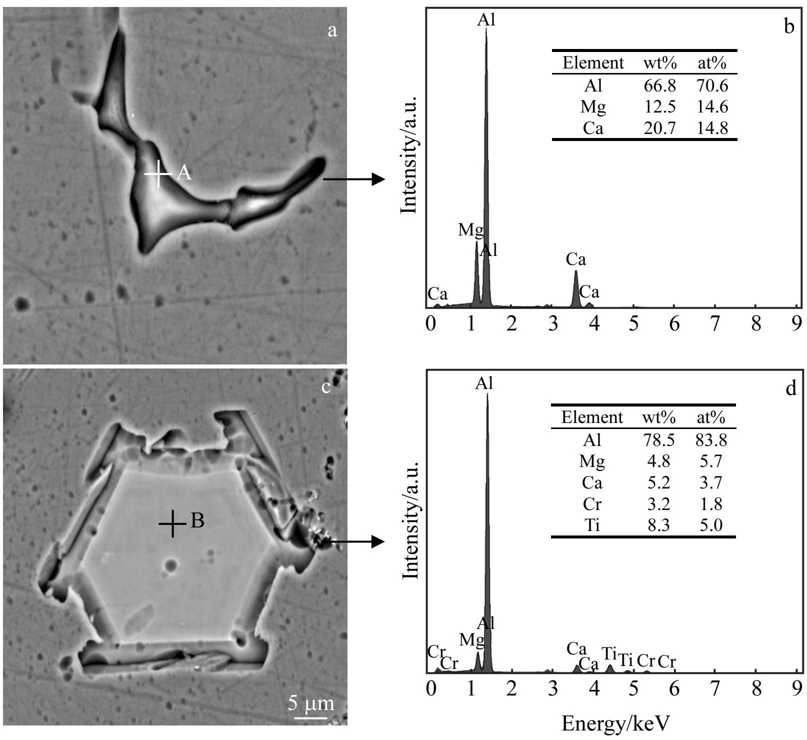

Fig.2 BSE images (a, c) and EDS spectra (b, d) at grain boundaries of the alloy (0.86 wt% Ca): (a, b) bar-like phase; (c, d) block-like phase

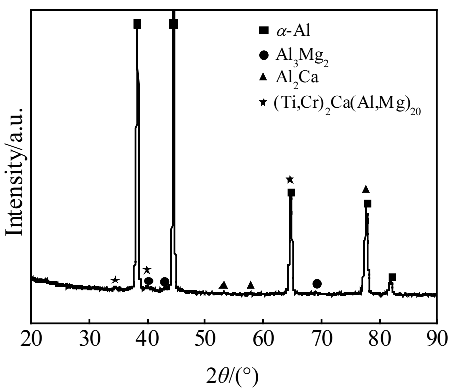

Fig.3 XRD pattern of the alloy (0.86 wt% Ca)

of Ca atoms grows, until the end of solidification. Content of Ca directly influence the degree of Ca enrichment on grain boundaries and the size of Ca-rich phase.

2.2 Mechanical properties

The Ca content has an influence on the composition of the grain boundary precipitation, and further affects the mechanical properties of alloys. Fig.4 shows some mechanical properties test results of the alloys with different Ca contents. In this study, tensile strength of the alloys first increases and then decreases with increasing Ca content, and the tensile strength reaches a maximum value (252.3 MPa) when the Ca content is 0.28 wt%, which means a small amount of Ca addition (less than 0.28 wt%) can enhance the tensile strength and excess Ca causes IMC gathering along grain boundaries and weakens the

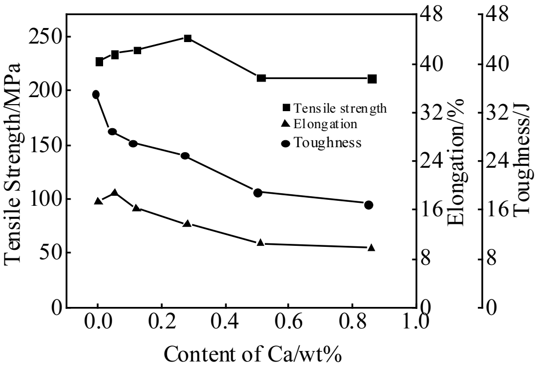

Fig.4 Effect of Ca content on mechanical properties of alloys

alloy. As for elongation ability and toughness, both characteristics decrease along with the increasing of Ca content, but it is noticeable that in both cases the change rate ascends after the Ca content exceeds 0.28 wt%. This point is critical for the coexistence of bar-like and block-like Ca-rich phases, exerting baneful influence on the mechanical properties of alloys.

2.2.1 Influence of Ca on tensile strength

Influence of Ca on the tensile strength can be simply expressed as $\Delta\sigma=\Delta\sigma_s+\Delta\sigma_g+\Delta\sigma_p$, wherein the strength $\Delta\sigma_s$ is due to the difference of solid solubility, the strength $\Delta\sigma_g$ is due to the difference of grain refinement, the strength $\Delta\sigma_p$ is due to the difference of phases of alloys. Although the matrix grains of six specimens are similar (Fig.1), the strength σ_g shows little difference. When the content of Ca is low (less than 0.28 wt%), Ca is primarily dissolved in the α-Al matrix, and solid solution strengthening (σ_s) plays a dominant role on the strength changes. When the Ca content is over 0.28 wt%, bar-like Al_2Ca and block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ combines together to exert baneful influence on $\Delta\sigma_p$ of the alloys. So when the alloy precipitates over a certain amount, the tensile strength decreases. Ca content of 0.28 wt% is the tensile strength transition critical point.

2.2.2 Influence of Ca on ductility

Fig.4 and 5 show that when the Ca content is lower than 0.28 wt%, the elongation of alloy decreases slightly with increasing Ca content; when the Ca content is higher than 0.28 wt%, the elongation decrease sharply. Fig.5a, 5b shows that the fracture morphology of the sample is dimple when the Ca content is lower than 0.28 wt%. When the Ca content is higher than 0.28 wt%, the number of dimples decreases and the Ca atoms can not dissolve in the Al matrix; thus they form compounds and gather along the grain boundaries. These nonuniformly distributed phases are brittle and thus cause stress concentration and intergranular micro-cracks (Fig.5c, 5d), which usually start a fracture and are baneful for alloy ductility. When the Ca content is higher than 0.28 wt%, block-like phase particles grow in size and amount and even more unevenly distributed, thus leading to worse ductility. Also when Ca content is higher than 0.28 wt%, discontinuous bar-like Al_2Ca phase particles appear at grain boundaries, which weaken the ductility of the alloys even further.

2.2.3 Influence of Ca on toughness

Fig.6 shows the appearances of the impact fracture surface of 0.00 wt% Ca and 0.28 wt% Ca specimens. When Ca is not added, the fracture has typical transgranular fracture characteristics. Lots of dimples and nucleation particles are observed (Fig.6a). When Ca content reaches 0.28 wt% (Fig.6b, 6c), the amount of dimples decreases significantly and cleavage planes appear in river pattern, and tear ridges also appear. Fractures are initiated by second phase particles (Fig.6c, arrow pointed), and the fracture shows apparent brittle cleavage fracture characteristics. When Ca content is higher than 0.28 wt%, the block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ and bar-like Al_2Ca particles are located on the grain boundaries coexist. Both of these phases are brittle and impedance of the deformation of specimens when the specimens are under impact loading,

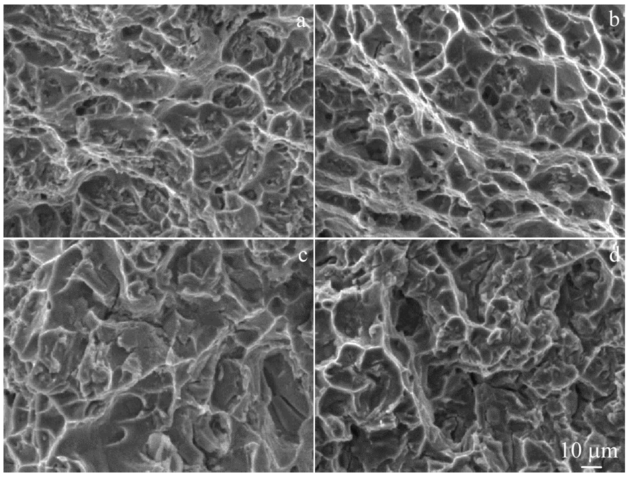

Fig.5 SEM fractographs of the tensile test alloys: (a) 0 wt% Ca, (b) 0.05 wt% Ca, (c) 0.28 wt% Ca, and (d) 0.51 wt% Ca

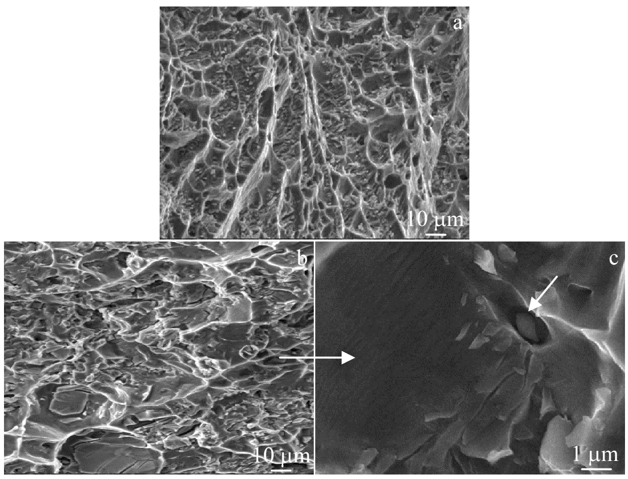

Fig.6 SEM fractographs of the impact test alloys: (a) 0 wt% Ca, (b) 0.28 wt% Ca, and (c) local magnification of Fig.6b

which cause dislocations to pile up and become the crack initiation, and then the cracks propagate into the matrix *α*-Al grains under stress and lead to brittle fracture. The nonuniformly distributed Al_2Ca second phase along the grain boundaries violates the continuity and uniformity of grain boundaries, which largely weakens the strength of the grain boundary and makes the matrix vulnerable to brittle cleavage fracture, thus decreasing the toughness of alloy. The coarse $(Ti,Cr)_2Ca(Al,Mg)_{20}$ grains and Al_2Ca particles are brittle and both incoherent with the matrix. These phases are broken under low stress and then easily become the fracture initiation and significantly decrease the impact toughness of theal loys.

When the Ca content is less than 0.28 wt%, a small amount of $(Ti,Cr)_2Ca(Al,Mg)_{20}$ inclusions in the alloy decrease the toughness slightly, but when the Ca content is over 0.28 wt%, bar-like Al_2Ca and block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ combines together to exert undesirable influence on the alloy toughness. To obtain a better mechanical property, the Ca content in the alloy should be controlled at 0.28 wt% or lower.

3 Conclusions

1) The phase composition of Al-5Mg alloy is changed by the Ca impurity. The block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ phase is distributed discontinuously along the grain boundaries when the Ca content is less than 0.28 wt%. When the content of Ca is over 0.28 wt%, bar-like Al_2Ca and block-like $(Ti,Cr)_2Ca(Al,Mg)_{20}$ combine together and are distributed along the grain boundaries, and the amount and size of Ca-rich phase (both the bar-like and block-like) increase with increasing Ca content.

2) Tensile strength of the Al-5Mg alloys increases firstly and then decreases with increasing Ca content, and the tensile strength gets to a maximum value when the content of Ca is 0.28 wt%. The plasticity and impact toughness decrease slowly (Ca content 0.00 wt%~0.28 wt%) but then significantly decrease (Ca content>0.28 wt%), and the tensile or impact fracture mode transforms from the transgranular ductile fracture to the brittle cleavage fracture.

3) To obtain a better mechanical property, the Ca content in the alloy should be controlled at 0.28 wt% or lower.

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杂质 Ca 对 Al-5Mg 填充合金凝固组织及力学性能的影响

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摘 要：结合拉伸试验和冲击试验，采用 SEM、EDS 和 XRD 等分析方法研究了杂质元素 Ca 对铝镁填充合金铸态凝固组织和力学性能的影响。结果表明，Ca 元素的存在改变了合金的相组成。当 Ca 小于 0.28%（质量分数，下同）时，合金中晶界富集有块状$(Ti,Cr)_2Ca(Al,Mg)_{20}$金属间化合物相。当 Ca 大于等于 0.28%时，块状$(Ti,Cr)_2Ca(Al,Mg)_{20}$相和不连续条状 Al_2Ca 相共同在晶界富集。随 Ca 含量的增加，合金中块状相和条状相尺寸逐渐增大，数量逐渐增加。合金抗拉强度随 Ca 元素的增加先升高后降低，Ca 含量为 0.28%时抗拉强度达到峰值。Ca 含量小于 0.28%时，合金塑性和冲击韧性随 Ca 含量增加缓慢下降，当 Ca 含量大于 0.28%时，合金塑韧性大幅下降。合金拉伸或冲击断口由穿晶延性断裂（Ca 含量<0.28%）转变为脆性断裂（Ca 含量>0.28%）。Ca 含量 0.28%为合金韧脆转变点。

关键词：Al-Mg 填充合金；Ca 含量；显微组织；力学性能

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