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Trans. Nonferrous Met. Soc. China 19(2009) 540-544

Transactions of Nonferrous Metals Society of China

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# Effect of Sc and Zr on microstructures and mechanical properties of as-cast Al-Mg-Si-Mn alloys

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Received 4 June 2008; accepted 4 October 2008

**Abstract:** Microstructures of as-cast Al-Mg-Si-Mn alloys with and without Sc and Zr were investigated by optical microscopy, scanning electronic microscopy(SEM) and energy dispersion spectrum analysis. Addition of 0.2%-0.4% Sc can refine the grain size and change the growth morphology from dendritic to fine equi-axial crystal. The higher the addition of Sc, the finer the as-cast grain size. The tensile strength is increased by more than 30% with 0.4% Sc. Moreover, an addition of 0.1%-0.2% Zr is able to refine grain size and change the growth morphology from dendritic to equi-axial grain too, but less effective. However, Zr is found to increase the ductility of the cast alloys, and the elongation is increased to 11.97% with 0.2% Zr.

Key words: Al-Mg alloy; Sc; Zr; microstructure; mechanical properties

# **1** Introduction

Aluminum alloys are widely used in fields of machinery, aviation, aerospace and automobile industries due to their low density, high strength and easy formability[1–2]. Among Al-Mg alloys, ZALMg5Si1Mn (ZL303) is not strengthenable by heat-treatment. Up to now, simple cast Al-Mg alloys have not been available because of their poor mechanical properties. To this point, it is very important and meaningful to produce Al-Mg cast alloys to meet the needs of application.

Alloying is one of the effective methods to make high performance cast aluminum alloys. Sc is one of the most micro-alloying elements for aluminum alloys[3–4]. For example, Al-5Mg alloy with 0.18% (mass fraction) Sc has a grain size of 30–80 µm compared with 100–300 µm without Sc addition[5]. The effect can be more remarkable by partially replacing Sc with Zr to produce intermetallic Al<sub>3</sub>(Sc,Zr) dispersoids[6–7]. A number of experiments have verified the feasibility of mixture of Sc and Zr[8–9] for wrought Al-Mg alloys. It is reported that Zr can be dissolved into Al<sub>3</sub>Sc lattice to a level about 50% to form Al<sub>3</sub>(Sc<sub>1–x</sub>Zr<sub>x</sub>) phase[10–11]. This new phase is similar to its parental Al<sub>3</sub>Sc phase with all beneficial effects being remained and offering a lower coarsening tendency at elevated temperature. It can then effectively refine grain size. However, the effects of Sc and Zr on microstructures and mechanical properties of as-cast Al-Mg-Si-Mn alloys have less been reported in the literatures.

In this work, the alloying effects of Sc and Zr on microstructures and mechanical properties of Al-Mg cast alloys were investigated in order to improve their mechanical properties.

## 2 Experimental

ZALMg5Si1Mn (symbolized as ZL303) is a typical Al-Mg alloy and its chemical compositions are listed in Table 1. As-cast ZL303 contains microstructure of  $\alpha$ (Al)+[ $\alpha$ (Al)+Mg<sub>2</sub>Si]. As a detrimental element, Si can form eutectic structure  $\alpha$ (Al)+Mg<sub>2</sub>Si to modify the castability without precipitation of Al<sub>3</sub>Mg<sub>2</sub>. ZALMg5Si1Mn alloy is thought to have higher mechanical properties at elevated temperatures because Mg<sub>2</sub>Si particles can restrain the deformation of the  $\alpha$ (Al) matrix. However, this alloy has limited mechanical properties at room temperature.

Table 1 Composition	of ZALMg5Si1	(mass fraction, %)	)
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Mg	Si	Mn	Al
4.5-5.5	0.8-1.3	0.1-0.4	Bal.

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Alloying with Sc and Zr elements is adopted in order to improve room temperature mechanical properties of ZALMg5Si1 alloy. The chemical compositions of the materials used in this work are listed in Table 2.

Table 2 Chemical composition of test alloys (mass fraction, %)

Alloy No.	Sc	Zr	Si	Mg	Mn	Al
0	-	_	0.80	5	0.4	Bal.
1	-	_	0.15	5	0.4	Bal.
2	-	0.1	0.50	5	0.4	Bal.
3	-	0.2	0.80	5	0.4	Bal.
4	0.2	_	0.50	5	0.4	Bal.
5	0.2	0.1	0.80	5	0.4	Bal.
6	0.2	0.2	0.15	5	0.4	Bal.
7	0.4	_	0.80	5	0.4	Bal.
8	0.4	0.1	0.15	5	0.4	Bal.
9	0.4	0.2	0.50	5	0.4	Bal.

The alloys were melted in a graphite crucible with lid covering to prevent magnesium from oxidization. Sc, Zr, Si and Mn were added to the melt using master alloys of Al-Sc, Al-Zr, Al-Si and Al-Mn, respectively. The melting temperature was kept as 750°C and the melt was gravity-cast into specimens in a metallic mould that was preheated to 200 °C. All the mechanical tests were carried out using a CSS1220 type electric universal tensile tester. Three specimens were tested and their average value was calculated as the result. Hardness was determined in a Brinell hardness tester. For metallography investigation, specimens were etched by a mixed-acid etchant and microstructure was observed using an optical microscope. The fracture surface of specimen was analyzed using an electric scanning microscope(SEM). The distribution of alloying elements in micro-area was determined with an energy dispersion scope.

#### **3 Results and discussion**

#### **3.1 Mechanical properties**

The mechanical properties and the hardness of the alloys are listed in Table 3 and Table 4, respectively. The results were orthogonal analyzed and it is shown that among Sc, Zr and Si, Sc has the strongest effect on tensile strength; Zr is the next; and the effect of Si is the weakest. In the case of effect on elongation, Si is the strongest, Zr the next, and Zr the weakest.

The results in Table 4 show that Sc has the strongest effect on hardness. Especially, alloy with 0.4% Sc shows 40% harder than normal ZL303 alloy. The ZL303 alloy **Table 3** Mechanical properties of Al-Mg-Si-Mn alloys

Alloy No.	$\sigma_{ m b}/{ m MPa}$	$\delta$ /%
0	220	4.10
1	229	11.13
2	233	8.40
3	233	11.97
4	245	11.39
5	238	6.70
6	241	14.36
7	287	5.00
8	303	14.81
9	279	4.60

Table 4 Hardiess of Al-Ivig-bi-Ivill alloys	Table 4	Hardness	of Al-Mg-Si-Mn	alloys
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	0		
Alloy No.	HBS	Alloy No.	HBS
0	66.0	5	73.2
1	67.7	6	76.3
2	65.0	7	92.3
3	64.6	8	89.7
4	77.1	9	80.6

with a lower silicon content of 0.8% was melted. The Alloy No.3 with an addition of 0.2% Zr compared with normal ZL303 alloy shows 6% increase in tensile strength and 192% increase in elongation. Alloy No.5 of 0.2% Sc and 0.1% Zr with respect to normal ZL303 alloy shows 8% increase in tensile strength and 63% increase in elongation. Alloy No.7 of 0.4% Sc shows 30% increase in tensile strength and 22% gain in elongation. The significant effect of Zr on elongation and tensile strength has been verified through these data.

Thinking about the content of silicon in the alloy, it should be limited at a level lower than 0.15% to obtain the strengthening effect of Sc. However, this may contradict to that required by castability, for which silicon is kept as high as 0.8% to improve the castability of ZL303. This work tried to find a combination to obtain both good mechanical properties and castability.

It is noticed that Alloy No.3 has good elongation and No.7 shows improved tensile strength. By decreasing the silicon content to 0.15%, Alloy No.1 gains a tensile strength only 4% higher than normal ZL303 alloy, while the elongation shows 171% improvement. By addition of Sc in Alloy No.6, 5% gain in tensile strength and 29% increase in elongation are obtained compared with alloy No.1, respectively. Additions of 0.4% of Sc and 0.1% of Zr in Alloy No.8 obtains 32% and 33% improvement in tensile strength and elongation, respectively. It is found that at lower silicon content, Sc plays a good alloying effect and is affected by the silicon content. From the data of alloys No.2 and 4, it is known that at 0.5% Si, an addition of 0.2% Sc to the alloy makes both higher tensile strength and elongation than an addition of 0.1% Zr. However, data of alloy No.9 shows an improvement in tensile strength but a decrease in elongation caused by a combination of 0.4% Sc and 0.2% Zr.

## 3.2 As-cast optical microstructures

The optical microstructures are shown in Fig.1. Obviously to Alloy No.3 an addition of 0.2% Zr can refine the grain size respecting to the normal ZL303 alloy (No.0) that shows coarse grains in developed dendrites. In contrast to alloy No.2, No.3 shows that increasing Zr from 0.1% to 0.2% can significantly reduce grain size even at higher Si level. An addition of 0.2% Sc to alloy No.4, the dendrite formation is restrained, while the grain size is refined. A combination addition of 0.1% Zr and 0.2% Sc can also significantly refine the grain size of alloy No.5. Refined grains in alloy No.7 with an addition of 0.4% Sc shows equi-axial grains of 5–35  $\mu$ m. SEM images of as-cast microstructure are shown in Fig.2 and Fig.3. Fig.2 shows the as-cast microstructure of alloy No.7 and square or triangular second phase particles with size of 5–8  $\mu$ m are found. With high levels of Al and Sc, these second phase particles are believed to be Al<sub>3</sub>Sc[8,12]. From Fig.3 square particles and Al, Sc and Zr are detected by EDS, so this phase is regarded as Al<sub>3</sub>(Sc, Zr)[10–11].

#### **3.3 Discussion**

According to the heterogeneous nucleation theory, the refinement of grain size of cast metals is determined by the number of nuclei in unit melt as well as their nucleating effectiveness. The effectiveness of the nuclei



Fig.1 Optical microstructures of Al-Mg-Si-Mn alloy samples: (a) No.0; (b) No.2; (c) No.3; (d) No.4; (e) No.5; (f) No.7

542



**Fig.2** SEM image (a) of second phase particles in alloy No.7 and EDS spectum (b) of square particle

depends on the relationship between the lattice types and parameters of the particle and  $\alpha$ (Al) matrix, while the similarity in lattice types plays an important role in grain refining.

It was reported[13–16] that eutectic reaction  $L \rightarrow \alpha$ (Al)+Al<sub>3</sub>Sc at 655 °C exists in Al side of Al-Sc binary system. The eutectics containing 0.52% Sc have a maximum solution in aluminum of 0.38%. With *L*12 type fcc lattice (AuCu<sub>3</sub> structure) and *a*=0.410 3 nm, similar to that of  $\alpha$ (Al) (*a*=0.408 8 nm)[14], Al<sub>3</sub>Sc may serve as heterogeneous nuclei during solidification to refine the grain size in as-cast structure.

Addition of Zr to Al-Mg alloy, Al<sub>3</sub>Zr can be precipitated directly from the melt at a low Zr content (w(Zr)>0.11%). Furthermore, the preferential precipitation of Al<sub>3</sub>Zr restrains coarse equilibrium Mg<sub>5</sub>Al<sub>8</sub> phase along the grain boundaries due to the strong affinity between Al and Zr[17]. A peritectic reaction  $L+Al_3Zr=\alpha(Al)$  follows in this system and  $\alpha(Al)$ forms around Al<sub>3</sub>Zr particles. Al<sub>3</sub>Zr has similar lattice parameters to Al and serves as effective heterogeneous nuclei for Al and refines the grain size [17]. These agree with the results in this work and can be verified by microstructures of alloys No.2 and 3. It was reported[16] that Al<sub>3</sub>(Sc<sub>1-x</sub>Zr<sub>x</sub>) or Al<sub>3</sub>(Sc, Zr) precipitates in Al-Sc-Zr

**Fig.3** SEM image (a) of square phase particle in alloy No.5 and EDS spectrum (b) of square particle

ternary system and these phases may be thought as substitutions on base of Al<sub>3</sub>Sc phase. A maximum fraction of 50% (molar fraction) can be reached by substituting parts of Sc atoms by Zr with similar lattice parameters. The mismatch between L12 type Al<sub>3</sub>Zr and  $\alpha$ (Al) is about 0.5%, while that between *L*12 type Al<sub>3</sub>Sc and  $\alpha$ (Al) is about 1.5%. Substituting Sc in Al<sub>3</sub>Sc by Zr may decrease the mismatch between the compound and  $\alpha$ (Al). This might increase the nucleating effectiveness and improve the grain fineness[15]. From Figs.1 and 2, we can see that primary Al<sub>3</sub>Sc and Al<sub>3</sub>(Sc, Zr) particle precipitates from the melt in a square or polygon form. These primary precipitated particles have high melting points and more stability, making them very ideal nuclei for refining the as-cast grain size of alloys and improving the mechanical properties. The higher the Sc content, the finer the grain size.

# **4** Conclusions

1) Among Sc, Zr and Si, Sc has the strongest effect on tensile strength; Zr is the next. Si has the strongest effect on elongation; Sc is the next while Zr is the weakest.

2) In order to strengthen the Al-Mg cast alloys by

addition of Sc and Zr, Si content should be limited to lower than 0.8%, to develop the strengthening effect of Sc to a full extent.

3) The improvement of mechanical properties of Al-Mg-Si-Mn cast alloys by adding Sc and Zr is due to the effect of fine-grain strengthening.

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(Edited by YANG Bing)