Rare Metal Materials and Engineering
Volume 50, Issue 3, March 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2021, 50(3): 0769-0774.

ARTICLE

Effect of Zr Content on Microstructures and Mechanical Properties of As-cast Al-Mn-Fe 3104 Alloy

Zhang Linhui, Zhong Binnian, Shi Dawen, Kang Xiaoshu, Ma Chaoyi

Qinghai Provincial Key Laboratory of New Light Alloys, Engineering Research Center of High Performance Light Metal Alloys and Forming, Qinghai University, Xining 810016, China

Abstract: The precipitation microstructure and mechanical properties of as-cast 3104 alloys with different Zr additions were investigated. The results show that the grain size of alloy decreases with the increase of Zr content, and the smallest grain (20 μm) is obtained when the Zr content ⩾0.25wt%. Meanwhile, the grain shape changes from feathery to equiaxed. Furthermore, Zr can improve the distribution of Si and Mn elements in the alloy by forming Si phase and other intermetallic compounds. Vickers hardness analysis shows that the addition of Zr reduces the hardness of Al-Mn-Fe 3104 alloy. Moreover, according to the results of tensile test, the tensile strength and elongation of the cast alloy increase with increasing the Zr content until Zr content reaches 0.25wt%. The proper content of Zr plays a role of pinning dislocation and preventing slip, which improves strength and toughness of the alloys.

Key words: zirconium; Al-Mn-Fe 3104 alloy; microstructure; mechanical properties

Al-Mn-Fe 3104 alloys are widely used in packaging industries[1-3], and become excellent tank material due to the low density (only 2.6 g/cm^3, about 1/3 as dense as copper or steel), superior corrosion resistance, high plasticity, good welding performance, and easy formability[4-6]. In industrial production, the cost of production materials can be saved by about 3% for every reduced 0.01 mm in thickness, so thickness decrease of material has become an upsurge in aluminum industry for energy saving. However, the yield dramatically reduces with decreasing the thickness[7]. So improving the mechanical properties of Al-Mn-Fe 3104 alloy is an urgent problem to be solved in alloy production.

Alloying is one of the effective methods to improve the performance of cast Al-Mn-Fe 3104 alloy. Mn, Fe, Si, Mg and Cu are the most important alloying elements in Al alloys. It is well-known that Mn is one of the reinforcing elements in commercial Al 3104 alloys[8] of a high content in the range from 0.05wt% to 1.6wt%. Mn in the alloy usually forms different phases ($MnAl_6$, $(MnFe)Al_6$), which decrease the welding performance. To allow for best performance, careful control of the Fe concentration in the alloy is essential because it is very beneficial to demould and reduce the segregation in grains[9,10]. At the same time, Fe forms different intermetallic phases (β-Al_5FeSi, α-$Al_{15}(MnFe)_3Si_2$), which decreases elongation to some extent. So primary alloys with lower Fe content and higher Mn content have been developed to overcome this problem. Besides, the enhancement effect of Mg is more effective than that of Mn[11], which reduces the crack tendency with a more favorable content from 0.2wt% to 2wt%. 0.1wt%~0.5wt% Si can improve the tensile capacity in production process of DI (drawn and ironed) cans[12,13] within a certain extent. Traditional strengthening precipitates with Mg and other alloying elements, such as Mg_2Si and α-$Al_{12}(FeMn)_3Si$, are generated[14-16]. Otherwise, 0.15wt%~0.20wt% Cu can improve the strength of 3104 alloy[17]. Al-Mn-Fe 3104 alloys in industry are selected components with optimal compatibility to meet the needs of application. Besides, the nanoscale Al_3Sc precipitates with high density (formed by Sc) and $Al_3(Sc, Zr)$ precipitates (substituted Sc in Al_3Sc by Zr) strengthen the mechanical properties

Received date: March 10, 2020
Foundation item: Aluminum Corporation of China Limited Qinghai Branch (K151879); Natural Science Foundation of Qinghai Province (2018-ZJ-957Q)
Corresponding author: Zhong Binnian, Ph. D., Qinghai Provincial Key Laboratory of New Light Alloys, Engineering Research Center of High Performance Light Metal Alloys and Forming, Qinghai University, Xining 810016, P. R. China, E-mail: bnzhong@qhu.edu.cn

and creep resistance of Al alloys[18-20], which has been paid much attention by researchers. However, few reports have been found on the microstructure and mechanical properties of cast Al-Mn-Fe 3104 alloys with the addition of Zr. According to Vončina[10], Zr can greatly improve the recrystallization temperature of aluminum alloy, as well as the strength, fracture toughness, quenching sensitivity and stress corrosion resistance of the alloy, which increases the nucleation rate of aluminum alloy and refines the grain of the alloy.

In this research, the microstructure and mechanical properties of cast Al-Mn-Fe 3104 alloys with different Zr additions were investigated, and the influence of Zr content on grain size, phases and mechanical properties was studied.

1 Experiment

The composition of Al-Mn-Fe 3104 alloys is listed in Table 1. The 3104 alloy is the base alloy prepared by industrial products. Zr powders (Zr purity⩾99.5wt%) were used as alloying agents.

The Al-Mn-Fe 3104 alloys ingots were melted at 750 °C in a 5 kg ceramic crucible using an electrical resistance furnace, and 0.1wt%, 0.15wt%, 0.2wt%, 0.25wt% and 0.3wt% Zr powders were added into the melt respectively. After they were completely melted, stirred and cleaned off, the melt was poured into a steel mold which was preheated to 200 °C. The casting (Φ40 mm, ~2 kg) was subsequently cut into pieces of 10 mm×10 mm×10 mm and dog-bone-shaped blocks by wire cutting machine. Each square specimen was polished and then etched by Keller's reagent at room temperature for about 40 s.

The microstructures of the specimens were examined by optical microscope (OM). The distribution of the elements in samples was investigated by energy dispersive spectrometer (EDS). The phase composition of Al-Mn-Fe 3104 alloys was measured by X-ray diffraction (XRD) analyzer. The Vickers micro-hardness of the sample was tested by the Vickers Indenter (HR-150B) at room temperature with a load of 200 g and a dwell time of 10 s. After the bone sample was polished, tensile experiments were carried out at room temperature using an Instron machine with a constant displacement rate of 0.5 mm/min. It was worth noting that the number of tested samples was 3~5 in this work.

Table 1 Composition of Al-Mn-Fe 3104 alloy (wt%)

Fe	Si	Cu	Mn	Mg	Al
0.3~0.5	0.17~0.23	0.16~0.23	0.8~1.0	1.2~1.28	Bal.

2 Results and Discussion

2.1 Effect of Zr content on microstructure of Al-Mn-Fe 3104 alloy

Fig.1 shows the OM microstructures of as-cast Al-Mn-Fe 3104 alloy with different Zr contents, and all the insets are the images obtained by enlarging the main images by 2.5 times. Fig.2 and 3 are SEM microstructures and EDS analyses of 3104 alloy without and with 0.2wt% Zr, respectively.

For comparison, the typical microstructure without Zr addition is also shown in Fig.1a. It can be seen from Fig.1 that the surfaces of the samples are of high density without obvious holes, and the grain boundaries are clear. The microstructures consist of intermetallic phases and aluminum cells. As shown in Fig.1, the intermetallic phases are in dark colors and distributed at the aluminum dendrite boundaries. Most of them are identified as Mg_2Si, Al(FeMn)Si and Al_6(FeMn)[16,21], the latter two of which exhibit coarse lamellar

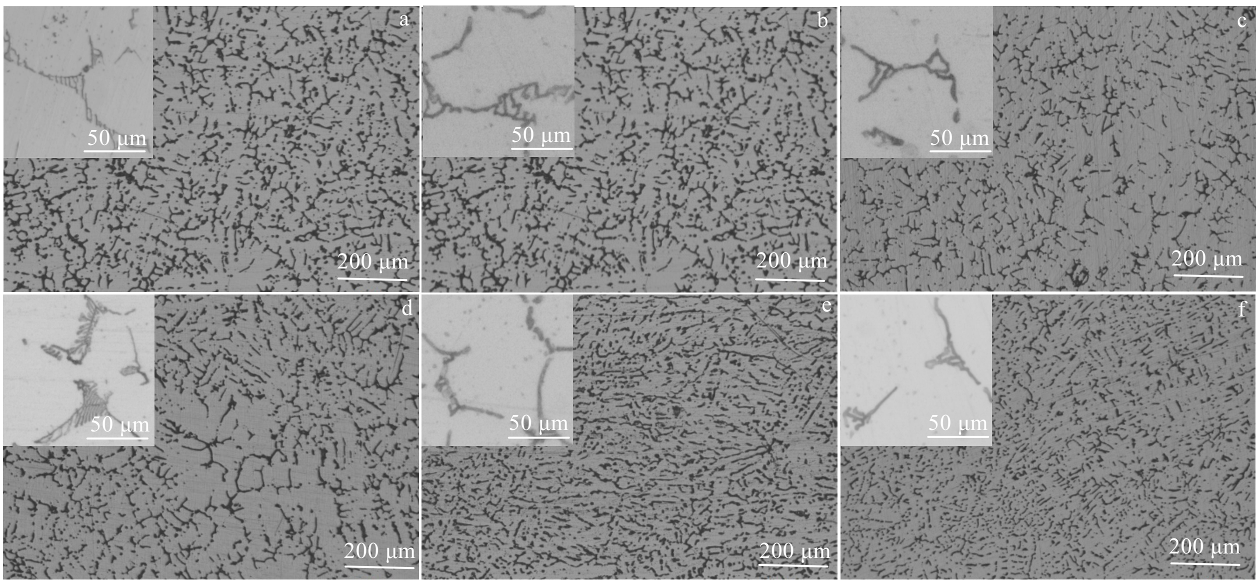

Fig.1 OM micrographs of Al-Mn-Fe 3104 alloys with different Zr additions: (a) 0wt%, (b) 0.10wt%, (c) 0.15wt%, (d) 0.20wt%, (e) 0.25wt%, and (f) 0.30wt%

and skeleton morphologies. For alloy without Zr addition (Fig.1a), the grain is petal-like, its size is uniform (about 30 μm), and the intermetallic phases account for a large volume fraction. From Fig.1b, with an addition of 0.1wt% Zr, the grain sizes tend to decrease. The lamellar and skeleton morphology decreases, so the branching occurs. In Fig.1c and 1d, the size of grains is smaller while the larger grains decrease significantly. When the Zr content is 0.25wt% and 0.30wt%, the shape of grains is regular of about 20 μm in size, as shown in Fig.1e and 1f, respectively. Meanwhile, the volume fraction of the intermetallic phases decreases. Obviously, adding Zr can reduce the size of grains[22]. But when the content of Zr is more than 0.25wt%, the grain size does not change. The smallest grain is about 20 μm, and the shape of phases which are distributed at the aluminum dendrite boundaries changes to needle-like shape. As the core of heterogeneous nucleation, Al_3Zr particles formed by Zr in the melt promotes the nucleation of α-Al. With the increase of Zr content, the number of Al_3Zr particles and heterogeneous nucleation increases, and the effect of grain refinement is more obvious. On the other hand, under the action of Al_3Zr, more fine α-Al equiaxed crystals form in the constitutional supercooling region at the front of the interface.

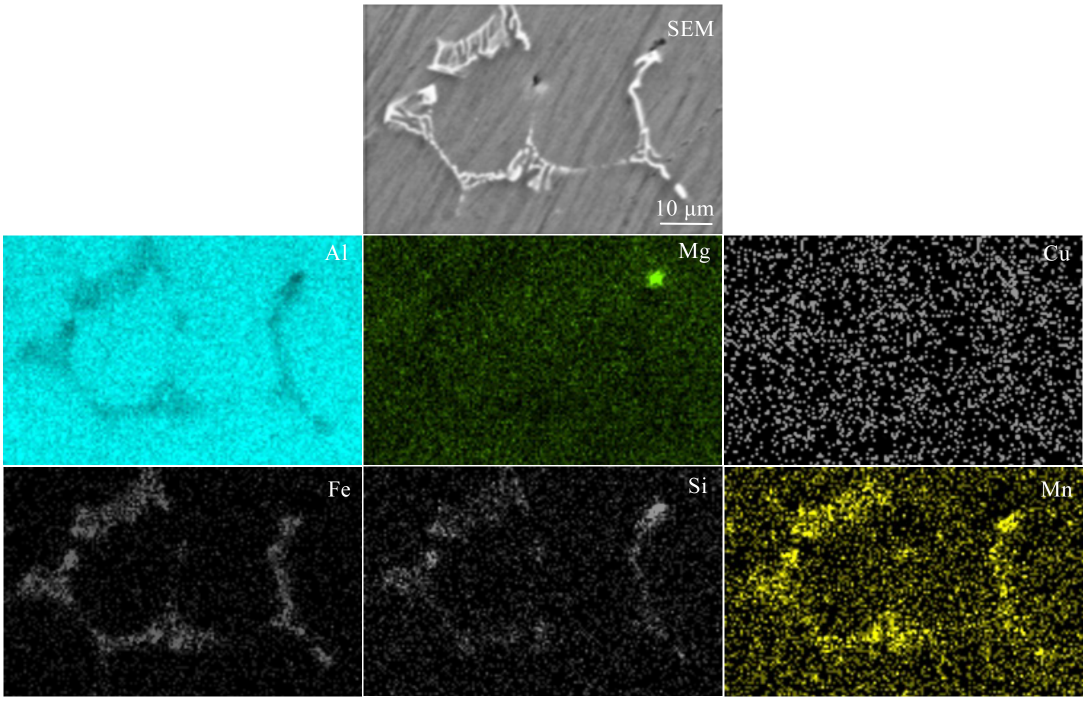

Fig.2 SEM microstructure and EDS analysis of industrial Al-Mn-Fe 3104 alloy without Zr

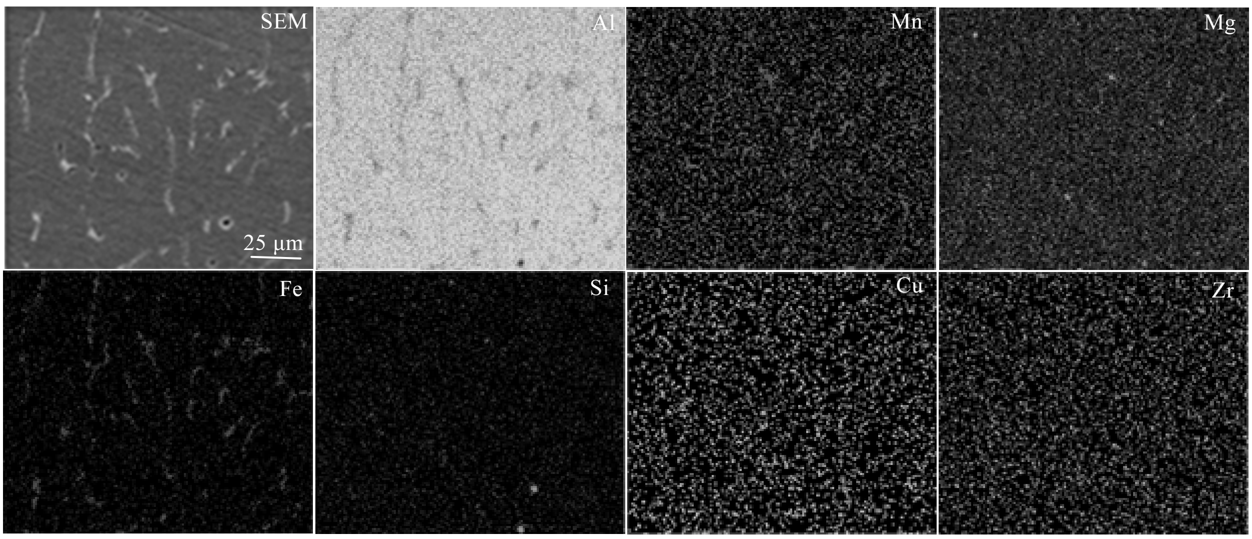

Fig.3 SEM microstructure and EDS analysis of 3104 aluminium alloy with 0.2wt% Zr

Fig.2 shows that under the cast condition, the 3104 alloy without Zr addition produced by industry has casting defects, and the intermetallic phases at the grain boundary have lamellar and skeleton morphology. The distribution of elements in Al-Mn-Fe 3104 alloy is irregular, except Cu. Mg and Al are mainly distributed in the crystal, while less at the grain boundary. Conversely, Mn, Fe and Si are more distributed at the grain boundary but less in the intergranular area. Therefore, the phases at the grain boundary are mainly composed of Mn, Fe and Si. The coarse plate-like phases, formed in intermetallic by Mn, Fe, Si and Al, tend to aggregate at the grain boundary of solidification, and the segregation phenomenon is obvious. There are larger Fe-rich phases in the intermetallic of 3104 ingot[23].

For 3104 alloy with 0.2wt% Zr addition, the distribution of Mn, Mg, Cu and Zr is relatively uniform, as seen in Fig.3. Al is still less distributed at the grain boundary than that in the commercial Al 3104 alloy. Distribution of Fe is observed at the grain boundary. In addition to segregation, the distribution of Si tends to be uniform. Compared to Fig.2, Zr content influences the distribution of Si the most, followed by Mg and Mn. During the solidification process of alloys, the eutectic Si always takes α-Al phase as the leading phase and grows coordinately with it. With the refinement of α-Al phase, the eutectic Si is correspondingly refined and its distribution improves. In addition, Zr has a high diffusion activation energy in Al, so its constituent phases are not easy to aggregate and grow. At a higher temperature, the phases still disperse in the crystal and at the grain boundary, affecting the distribution of elements.

Fig.4 shows the XRD patterns of Al-Mn-Fe 3104 alloys with different Zr contents. The XRD patterns of the alloy show that α-Al is the most obvious phases presented in the microstructure. With increasing the Zr content, Si phase increases. When Zr content is high, the orientation of crystal grains changes. Because of high activity, Zr, Al, Mn, and Mg elements are easy to form Zr-containing compounds with complex composition and morphology, which cannot be shown due to their small amount.

2.2 Effect of Zr content on mechanical properties of Al-Mn-Fe 3104 alloy

Fig.5 shows the micro-hardness of Al-Mn-Fe 3104 alloy with different Zr additions. The hardness of Al-Mn-Fe 3104 alloy without Zr addition is about 700 MPa. However, a sharply decrease of hardness is found after adding 0.1wt% Zr (~600 MPa, decreased by 14% comparing with the alloy without Zr addition). However, with the increase of Zr content, the hardness of 3104 alloy increases. The alloy containing 0.25wt% Zr shows the highest hardness of 710 MPa which equates the hardness of alloy without Zr. When the Zr addition is greater than 0.25wt%, the hardness of alloys reduces. With the addition of Zr, the phase in the alloy is homogenized, but the effect of grain refinement is not obvious, which leads to the decrease of the hardness of the alloy. With the increase of zirconium content, the grain refinement[23,24] and the increase of Si/Fe rich phase improve the hardness of the alloy. When the mass fraction of Zr is too high, Si and some intermetallic compounds increase, which promotes the crack formation in ingot. In addition, the displacement solid solution caused by Zr also affects the hardness of the alloy. It suggested that Zr additions may have no positive effect on the hardness of as-cast Al-Mn-Fe 3104 alloy, or even reduce the hardness. This is consistent with the statement in Ref.[10].

The tensile strength and elongation results are shown in Table 2 for the Al-Mn-Fe 3104 alloy with different Zr additions at room temperature. Three tests were performed on each material to ensure the accuracy of tensile test data. Obviously, with increasing the Zr addition, the tensile strength of the alloys gradually increases. The tensile strength of the industrial product without Zr is 173 MPa. The maximum tensile strength of the alloy is 185 MPa when the alloy contains 0.25wt% Zr, and the elongation is about 25%. The maximum elongation of the samples is 29% with the Zr addition of 0.25wt%, but deceases with excessive Zr (0.3wt%). When the addition of Zr is 0.25wt%, the grain size reduces and mechanical properties improve. At

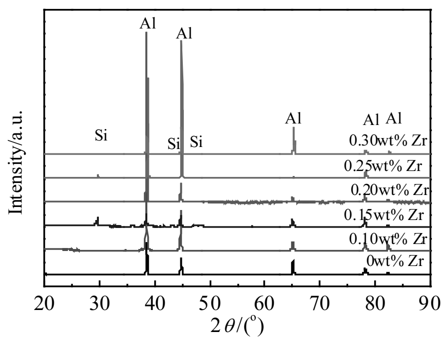

Fig.4 XRD patterns of the Al-Mn-Fe 3104 alloys with different Zr contents

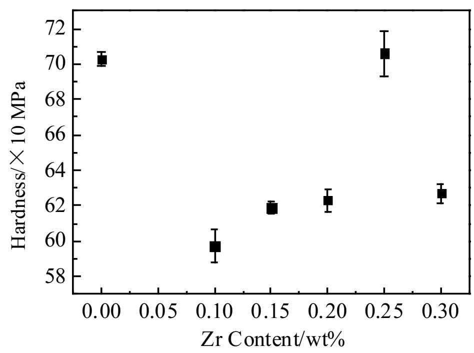

Fig.5 Vickers micro-hardness of Al-Mn-Fe 3104 alloys with different Zr contents

Table 2 Mechanical properties of 3104 alloy with different Zr contents

Zr content/wt%	0	0.10	0.15	0.20	0.25	0.30
Tensile strength/MPa	173±3	175±5	179±3	180±2	185±2	185±3
Elongation/%	25±0.1	26±0.1	27±0.2	28±0.1	29±0.2	27.5±0.1

higher levels of Zr, however, the grain size and tensile strength are almost unchanged, but the elongation decreases.

Al_3Zr phase dispersing in the crystal and at the grain boundary has the effect of pinning dislocation, hindering the migration of grain boundary, inhibiting recrystallization of the alloy, strengthening structure and precipitation of the alloy, improving the strength and maintaining high toughness of the alloy. But when the mass fraction of Zr is too high, the amount of Si phase and Fe-rich phase increases. They are brittle phases, which are easy to become the crack source during the process of material deformation, increasing the tendency of crack formation in ingot, and reducing the toughness of material.

Otherwise, the addition of Zr in Al alloy causes the precipitation to start at a lower temperature during aging and the recrystallization to start at an elevated temperature[25,26], which needs to be further proved.

3 Conclusions

1) With increasing the Zr content, the grain size of the alloys gradually decreases, and an addition of 0.25wt% Zr can refine the grain size of Al 3104 alloy. The significant effect of Zr addition on improving element distribution has been verified. The Si phases in alloy increase with the increase of Zr content.

2) Zr has no positive effect on the hardness of as-cast Al-Mn-Fe 3104 alloy. When the content of Zr in the material is 0.25wt%, the alloy hardness is close to that of the material without Zr. As Zr content is 0.1wt%, 0.15wt%, 0.20wt%, and 0.30wt%, the hardness of the material shows a decline trend compared with the hardness of material without Zr.

3) The tensile strength of the alloy increases gradually with increasing the Zr content, and the elongation increases within a certain Zr content range.

References

1 Huang R Y, Yin Z M, Huang Q W *et al*. *Advanced Materials Research*[J], 2012, 535-537: 987

2 Rękas A, Latos T, Budzyn R *et al*. *Key Engineering Materials*[J], 2015, 641: 246

3 Andrianov A V, Kandalova E G, Aryshensky E V *et al*. *Key Engineering Materials*[J], 2016, 684: 398

4 Aryshenskii E V, Aryshenskii V Y, Beglov E D. *Metal Science and Heat Treatment*[J], 2014, 56(1): 14

5 Zhen F, Sun J, Li J. *High Temperature Materials and Processes*[J], 2016, 35(6): 599

6 Zhang X M, Chen W P. *Transactions of Nonferrous Metals Society of China*[J], 2015, 25(6): 1715

7 Lin Mingshan. *Die & Mould Manufacture*[J], 2007(7): 27 (in Chinese)

8 Becker H, Bergh T, Vullum P E *et al*. *Materialia*[J], 2019, 5: 100 198

9 Liu C L, Du Q, Parson N C *et al*. *Scripta Materialia*[J], 2018, 152: 59

10 Vončina M, Medved J, Kores S *et al*. *Materials Characterization*[J], 2019, 155: 109 820

11 Yang H L, Ji S X, Yang W C *et al*. *Materials Science and Engineering A*[J], 2015, 642: 340

12 Buchanan K, Colas K, Ribis J *et al*. *Acta Materialia*[J], 2017, 132: 209

13 Mandal P K, Robi P S. *Materials Science and Engineering A*[J], 2018, 722: 99

14 Biffi C A, Fiocchi J, Tuissi A. *Journal of Alloys and Compounds*[J], 2018, 755: 100

15 Tao G H, Liu C H, Chen J H *et al*. *Materials Science and Engineering A*[J], 2015, 642: 241

16 Li Z, Zhang Z, Chen X G. *Materials Science and Engineering A*[J], 2017, 708: 383

17 Chakrabarti D J, Laughlin D E. *Progress in Materials Science*[J], 2004, 49(3-4): 389

18 Li Z, Zhang Z, Chen X G. *Materials Science and Engineering A*[J], 2018, 729: 196

19 Tzeng Y C, Jian S Y. *Materials Science and Engineering A*[J], 2018, 723: 22

20 Yang C, Shao D, Zhang P *et al*. *Materials Science and Engineering A*[J], 2018, 717: 113

21 Liu K, Chen X G. *Mater Des*[J], 2015, 84: 340

22 Dang J, Huang Y, Cheng J. *Transactions of Nonferrous Metals Society of China*[J], 2009, 19(3): 540

23 Lu F Y, Zang J L, Yu H *et al*. *Transactions of Materials and Heat Treatment*[J], 2017, 38(3): 54 (in Chinese)

24 Tian N, Yuan F, Duan C *et al*. *Materials*[J], 2019, 12(15): 2368

25 Dorin T, Ramajayam M, Babaniaris S *et al*. *Materialia*[J], 2019, 8: 100 437

26 Jo M S, Cho Y H, Lee J M *et al*. *Intermetallics*[J], 2020, 117: 106 667

锆对铸造 3104 铝合金微观结构和力学性能的影响

张林慧，仲斌年，时大雯，康啸殊，马超毅

(青海大学 高性能轻金属合金及成形工程研究中心 青海省新型轻合金重点实验室，青海 西宁 810016)

摘 要：研究了不同锆添加量的 3104 合金的析出组织和力学性能。结果表明，随着 Zr 含量的增加，合金晶粒尺寸减小，当 Zr 质量分数大于或等于 0.25%时，合金晶粒最小（20 μm）。同时，晶粒形状由羽毛状变为等轴状。此外，Zr 还可以通过形成 Si 相和其它金属间化合物来改善合金中 Si 和 Mn 元素的分布。维氏硬度分析表明，Zr 的加入会降低 Al-Mn-Fe 3104 合金的硬度。此外，根据拉伸试验结果，当 Zr 质量分数不高于 0.25%时，随着 Zr 含量的增加，合金的抗拉伸强度和延伸率都有所提高。适当的 Zr 含量可以起到钉扎位错和阻碍滑移的作用，提高合金的强度和韧性。

关键词：锆；Al-Mn-Fe 3104铝合金；微观结构；力学性能

作者简介：张林慧，女，1987 年生，博士，讲师，青海大学高性能轻金属合金及成形工程研究中心，青海 西宁 810016，电话：0971-5315838，E-mail: zhanglinhuia@126.com