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Effect of Al-5Ti-1B-xCe Refiner on Microstructure and Mechanical Properties of Cast Al-5Mg-3Zn-1Cu Alloys

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Abstract: The effects of Ce content on the microstructure and phase composition of the Al-5Ti-1B refiner and the refining effect of the Al-5Ti-1B-xCe (x = 0, 1, 5, 10 wt.%) refiner on the grain size, microstructure, and mechanical properties of Al-5Mg-3Zn-1Cu alloys were studied. The results show that the addition of 1.0 wt.% Ce in the Al-5Ti-1B refiner changes the TiAl₃ phase from block to strip, and the massive Ti₂Al₂₀Ce phase is formed. When the Ce content of the Al-5Ti-1B refiner increases to 5.0 wt.%, the plate-like TiAl₃ phase is surrounded by the Ti₂Al₂₀Ce phase, and the reticulate Al₄Ce phase is formed. With the Ce content of the Al-5Ti-1B refiner further increasing to 10.0 wt.%, a lot of network distribution Al₄Ce phase is formed. The volume of the Mg₃₂(AlCuZn)₄₉ phase of the as-cast Al-5Mg-3Zn-1Cu alloys is reduced after refining with the Al-5Ti-1B-xCe refiner. The Al-5Ti-1B-1Ce refiner has the best refining effect on as-cast Al-5Mg-3Zn-1Cu alloys, and the grain size of as-cast Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-1Ce refiner is reduced by 43% compared with as-cast Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner. Compared to the aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner, the yield strength, ultimate tensile strength, and fracture elongation of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner are improved by 4.0%, 4.6%, and 25.6%, respectively. Therefore, it can be seen that Al-5Ti-1B-1Ce refiner and Al-5Ti-1B-5Ce refiner have broad application prospects.



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Keywords: cast Al-5Mg-3Zn-1Cu alloys; Al-5Ti-1B-xCe refiner; tensile strength; refinement

1. Introduction

Al-Mg-Zn-Cu alloys are extensively utilized in the aerospace and automotive industries due to their high specific strength and superior overall properties [1–3]. The conventional Al-Mg-Zn-Cu alloy is a typical wrought Al alloy with excellent mechanical properties, but the lengthy and complicated deformation process raises the production cost and limits its application fields [4–6].

Undesirable dendritic segregation and coarse intermetallic particles can be observed in the as-cast Al-Zn-Mg-Cu alloy, which has adverse effects on the mechanical properties [7–9]. Therefore, Al-Mg-Zn-Cu alloy requires solution treatment and aging treatment to improve its strength. According to the difference in the Zn/Mg atomic ratio, there are the following three aging strengthening mechanisms: when the atomic ratio of Zn/Mg < 1, the precipitated strengthened phase is T' phase (Mg₃₂(Al, Zn)₄₉) [10,11]; when the atomic ratio of Zn/Mg > 2, the enhanced phase is η phase (MgZn₂) [12,13]; and when the Zn/Mg ratio is between 1 and 2, there will be co-precipitation strengthening effects [14,15]. Our previous

research found that the strength and fracture elongation of the Al-5Mg-3Zn-1Cu alloys after aging treatment are 518 MPa and 7.6%, respectively [16–19].

A grain refiner can improve the strength, plasticity, corrosion resistance, hardness, and casting performance of aluminum alloy, which highlights the necessity of studying aluminum alloy grain refiners [20]. The commonly used refiner for Al-Mg-Zn-Cu alloy is the Al-5Ti-1B refiner, but the TiB₂ particles in the Al-5Ti-1B refiner are easy to agglomerate, thus reducing the refining effect [21–23]. Therefore, it is necessary to develop a more efficient Al-Mg-Zn-Cu alloy refiner. Studies have shown that the addition of a rare-earth (RE) element can make the distribution of the TiB₂ phase in the Al-5Ti-B refiner more uniform, and improve the refining effect of the Al-5Ti-B refiner [24–26]. Wang et al. studied the effect of the Al-Ti-B-RE refiner on the mechanical properties of Al-7.0Si-0.55Mg alloy, and the results showed that the mechanical properties of Al-7.0Si-0.55Mg alloy reached the peak when the addition of the Al-5Ti-1B-3.0RE refiner was 0.2 wt.% [27]. The above materials are weight percentage (wt.%), and the materials below are weight percentage without special instructions. Meng et al. found that the grain refiner Al-5Ti-B-Ce can effectively refine the grain of 6111 alloys, improve grain refinement efficiency, and improve the strength and ductility of 6111 aluminum alloys [28].

There is scarce research on the effect of rare-earth content on the microstructure of the Al-5Ti-1B refiner and the effect of Al-5Ti-1B-xCe on the refining effect of Al-Mg-Zn-Cu alloy. Therefore, the effect of Ce content on the microstructure of Al-5Ti-1B-xCe and the effect of Al-5Ti-1B-xCe on the microstructure and mechanical properties of Al-5Mg-3Zn-1Cu alloys were studied in this paper.

2. Materials and Methods

2.1. Preparation of As-Cast Al-5Mg-3Zn-1Cu Alloys

The raw materials used for the preparation of Al-5Mg-3Zn-1Cu alloys are pure aluminum, pure magnesium, pure zinc, Al-50Cu master alloy, Al-5Ti-1B, Al-5Ti-1B-1Ce, Al-5Ti-1B-5Ce, and Al-5Ti-1B-10Ce. The above number in front of the elements is weight percentage (wt.%), and all mass percentages in this paper are weight percentages unless otherwise specified. Al-5Mg-3Zn-1Cu alloys are smelted in a high-temperature resistance furnace, the crucible used for smelting is an iron crucible, when the alloy melt is 730 °C, refiner is added, stirred evenly, and held for 15 min before casting. The types and mass fractions of refiners added to the alloy are shown in Table 1. The dimensions of the casting are shown in Figure 1a:

Table 1. Types and amounts of refiner added to Al-5Mg-3Zn-1Cu alloys (wt.%).

	Refiner	Mass Fraction of Refiner
1	Without refiner	0.0
2	Al-5Ti-1B	0.5
3	Al-5Ti-1B-1Ce	0.5
4	Al-5Ti-1B-5Ce	0.5
5	Al-5Ti-1B-10Ce	0.5

The samples were solid solution treated at 470 °C for 12 h, followed by water quenching at 15 °C. Subsequently, the samples were naturally aged for 168 h, and then aged in an oil bath at 150 °C for 12 h.

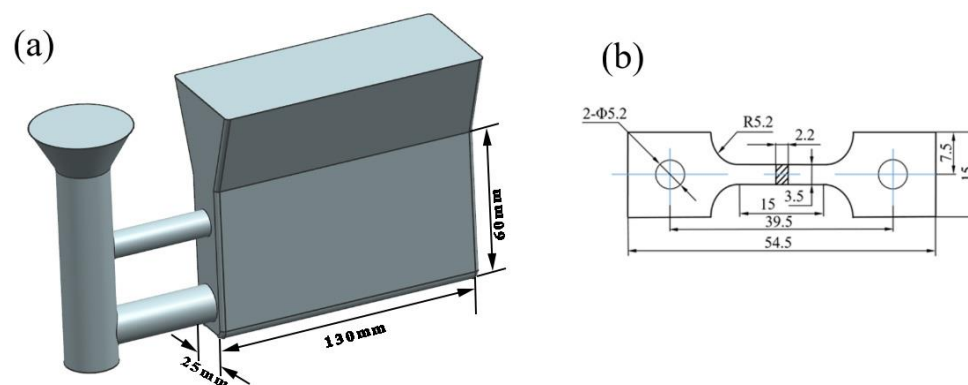


Figure 1. Size of castings and tensile specimen: (a) 3D model of the casting, (b) dimensions of the tensile specimen.

2.2. Phase Identification and Microstructure

Multifunctional X-ray diffractometer (XRD, D8 ADVANCE Da Vinci produced by Bruker GMBH in Bremen, Germany) was used to analyze the phase of the refiner and Al-5Mg-3Zn-1Cu alloys, and Jade 6 was used to calibrate the phase of the XRD diffraction spectrum. In diffraction analysis, the Cu target was used as the anode, the incoming ray was the $K\alpha$ ray of the Cu target, the scanning voltage was 25 kV, the scanning speed was $4^\circ/\text{min}$, and the scanning angle was $10\sim 90^\circ$.

The anode-coated samples were observed in polarizing mode on a ZEISS Axio Observer A1 optical microscope to distinguish the grains. The reagent used for anode coating is 2.5 vol.% fluoroboric acid and 97.5 vol.% water, the coating voltage is 20 V, and the coating time is 90 s. The software Image-Pro Plus 6.0 of Media Cybernetics was used to measure the grain size.

Scanning electron microscopy (SEM, JEOL JSM-7800F, NOVA NanoSEM 230 produced by Carl Zeiss in Berlin, Germany) was used to observe the microstructure of the alloy, and Energy Dispersive Spectroscopy (EDS) was used to analyze the composition of the phase.

2.3. Tensile Test

WDW-10S tensile testing machine was used to test the tensile properties of the samples, the dimension of the tensile samples was shown in Figure 1b, and the tensile speed was 0.02 mm/min. At least 3 parallel specimens were tested for each state to ensure data repeatability, and the average value was taken as the result of tensile properties. After the test, the tensile fracture of the specimen was observed by SEM.

3. Results and Discussion

3.1. Effect of Ce Content on Phase Composition and Microstructure of Al-5Ti-1B Refiner

Figure 2 shows the XRD patterns of the Al-5Ti-1B-xCe ($x = 0, 1, 5, 10$) refiner. The peaks of α -Al phase, TiAl_3 phase, and TiB_2 phase can be observed in Figure 2a. In addition to the peaks of the α -Al phase, TiAl_3 phase, and TiB_2 phase, the peaks of $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase are also observed in Figure 2b, meaning that $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase is formed in the Al-5Ti-1B-1Ce refiner. In Figure 2c,d, the peaks of the α -Al phase, TiAl_3 phase, TiB_2 phase, $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase, and Al_4Ce phase are observed and the peaks of the Al_4Ce phase in Figure 2d are higher than the peaks of the Al_4Ce phase in Figure 2c. The results indicated that the Al_4Ce phase was formed in the Al-5Ti-1B-xCe refiner with the increase in Ce content, and the amount of the Al_4Ce phase in Al-5Ti-1B-xCe increased with the increase in Ce content.

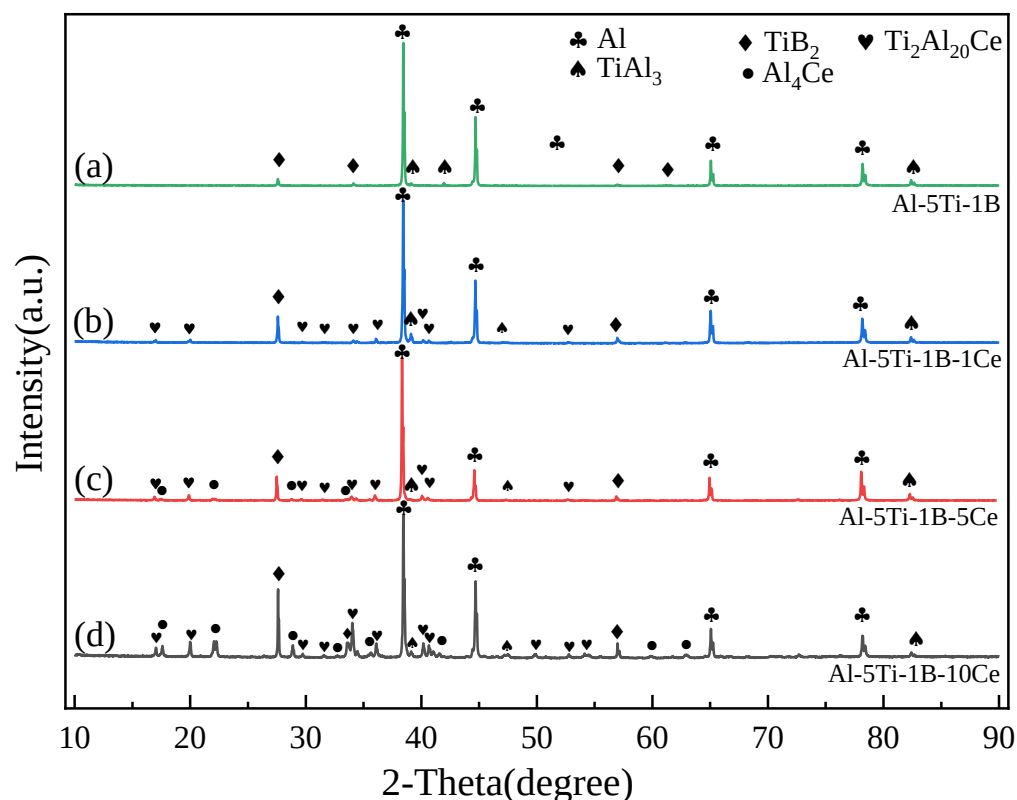


Figure 2. XRD patterns of the refiner: (a) Al-5Ti-1B, (b) Al-5Ti-1B-1Ce, (c) Al-5Ti-1B-5Ce, (d) Al-5Ti-1B-10Ce.

Figure 3 shows the optical microstructure and the SEM morphologies of Al-5Ti-1B, Al-5Ti-1B-1Ce, Al-5Ti-1B-5Ce, and Al-5Ti-1B-10Ce. Figure 3(e2–e4) show the element distribution of the EDS line scan at the arrow in Figure 3(e1). Table 2 shows the EDS results of Al, Ti, B, and Ce elements in Figure 3(a2–d2). Combined with EDS results in Table 2, it can be seen from Figure 3(a1,a2) that the point a1,a2 and a3 are α -Al matrix, TiB_2 granular phase, and blocky TiAl_3 phase, respectively. When 1 wt.% of Ce is added to Al-5Ti-1B, the blocky TiAl_3 phase changes to strip shape, and the blocky $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase is formed. It can be seen from Figure 3(b1,b2) that the point b1, b2, b3 and b4 are α -Al matrix, TiB_2 granular phase, lath-shaped TiAl_3 phase and blocky $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase, respectively. With a further increase in Ce content of the Al-5Ti-1B-xCe refiner, the size of the TiAl_3 phase increases, and a layer of the $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase shell is formed on its surface. In addition, with the increase in Ce content of the Al-5Ti-1B-xCe refiner, the amount of the $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase decreased and the amount of the Al_4Ce phase increased. It can be seen from Figure 3(c1,c2) that the point c1, c2, c3, c4, c5 and c6 are α -Al matrix, TiB_2 granular phase, lath-shaped TiAl_3 phase, $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase shell, blocky $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase and Al_4Ce phase, respectively. And the point c1, c2, c3, c4, c5 and c6 in Figure 3(c1,c2) are α -Al matrix, TiB_2 granular phase, lath-shaped TiAl_3 phase, $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase shell, bulky Al_4Ce phase and reticular Al_4Ce phase, respectively.

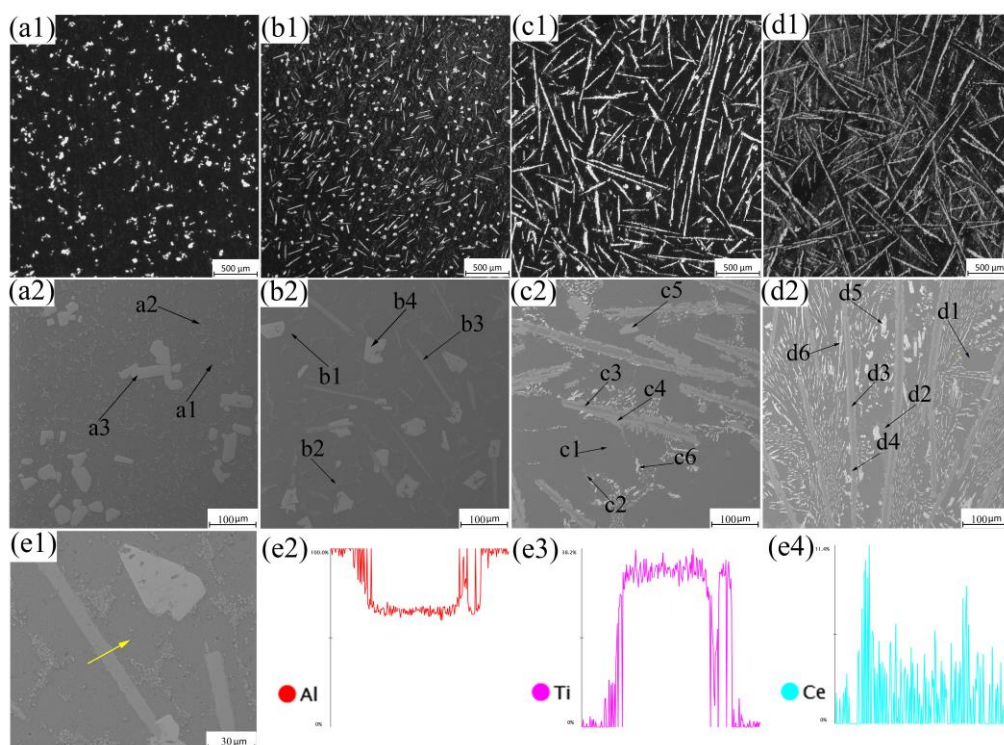


Figure 3. Microstructure of (a1,a2) Al-5Ti-1B, (b1,b2,e1) Al-5Ti-1B-1Ce, (c1,c2) Al-5Ti-1B-5Ce, (d1,d2) Al-5Ti-1B-10Ce, (e2–e4) are element distribution along the arrow in figure (e1).

Table 2. EDS analysis results of the refiner.

Refiner	EDS Position	Elements (at.%)			
		Al	Ti	B	Ce
Al-5Ti-1B	a1	99.79	0.21	0.00	0.00
	a2	53.56	25.23	21.21	0.00
	a3	78.48	21.16	0.35	0.00
Al-5Ti-1B-1Ce	b1	99.79	0.21	0.00	0.00
	b2	67.89	17.01	15.01	0.10
	b3	79.55	20.40	0.00	0.05
	b4	89.21	7.91	0.27	3.33
Al-5Ti-1B-5Ce	c1	99.69	0.05	0.25	0.00
	c2	67.89	17.01	15.01	0.10
	c3	79.22	20.78	0.00	0.00
	c4	88.83	7.83	0.24	3.55
	c5	89.36	7.05	0.00	3.59
	c6	81.45	0.78	0.20	17.57
Al-5Ti-1B-10Ce	d1	98.30	0.65	1.04	0.00
	d2	60.69	14.59	21.14	3.58
	d3	78.99	20.66	0.21	0.15
	d4	89.01	7.37	0.15	3.46
	d5	62.76	20.00	4.55	12.69
	d6	81.54	0.31	0.00	18.15

The element line distribution at the arrow on the strip phase In Figure 3(e1) is shown in Figure 3(e2–e4). From the element distribution, it can be seen that the Ce element on both sides of the strip is higher and the Ti element in the middle is higher, indicating that there is Ce atom enrichment on the surface of the strip TiAl_3 phase.

The change process of the TiAl_3 phase in Al-5Ti-1B-xCe with the increase in Ce content is shown in Figure 4. It can be seen from Figure 3 that the TiAl_3 phase in the Al-5Ti-1B refiner is blocky, while the TiAl_3 phase in the Al-5Ti-1B-1Ce refiner is shaped like a strip, and some Ce atoms are distributed around the TiAl_3 phase. Ce atoms adsorbed on the surface of the Al_3Ti phase will reduce the surface energy of the Al_3Ti phase, so Ce atoms in the Al-5Ti-1B-Ce refiner will spontaneously congregate onto the surface of the Al_3Ti phase [29]. The results show that when 1.0 wt.% Ce is added to the Al-5Ti-1B refiner, Ce atoms tend to adsorb to the surface of the TiAl_3 phase, and the large TiAl_3 phase transforms into a strip-like TiAl_3 phase, as shown in Figure 4b. With the increase in Ce content of the Al-5Ti-1B-xCe refiner, more Ce atoms gather on the surface of the TiAl_3 phase, and at the melting temperature of 713 °C, the peritectic reaction occurs on the interface between TiAl_3 and Ce atoms: $\text{Ce(L)} + \text{TiAl}_3(\text{S}) \rightarrow \text{Ti}_2\text{Al}_{20}\text{Ce(S)}$, thus forming a $\text{Ti}_2\text{Al}_{20}\text{Ce}$ shell on the surface of the TiAl_3 phase [30,31]. Therefore, there is a layer of $\text{Ti}_2\text{Al}_{20}\text{Ce}$ shell on the surface of the TiAl_3 phase in the Al-5Ti-1B-5Ce refiner, as shown in Figure 4c.

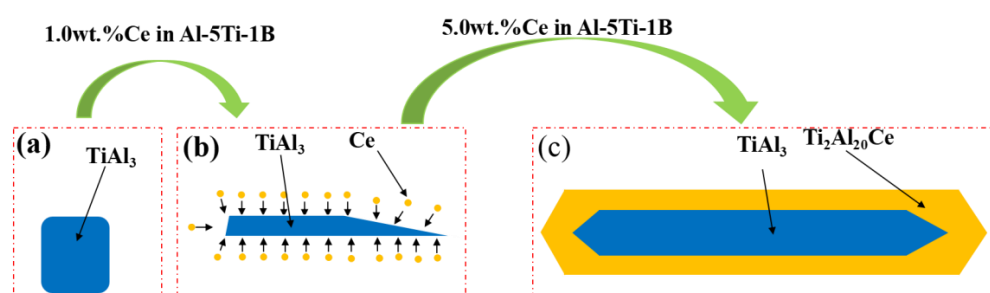


Figure 4. Schematic diagram of the effect of Ce content on the TiAl_3 phase in Al-5Ti-1B-xCe. (a) Al-5Ti-1B, (b) Al-5Ti-1B-1Ce, (c) Al-5Ti-1B-5Ce.

Figure 5 shows the SEM morphologies of TiB_2 in Al-5Ti-1B, Al-5Ti-1B-1Ce, Al-5Ti-1B-5Ce, and Al-5Ti-1B-10Ce. It can be seen from the figure that the TiB_2 phase in the Al-5Ti-1B refiner and the Al-5Ti-1B-1Ce refiner is a mesh distribution of particles with a diameter of about 1 μm . In Al-5Ti-1B-5Ce refiners and Al-5Ti-1B-10Ce refiners, TiB_2 is mainly distributed around the Al_4Ce phase, and the size of TiB_2 is about 2–3 μm . It can be seen that with the increase in Ce content of the Al-5Ti-1B-xCe refiner, the size of TiB_2 increases.

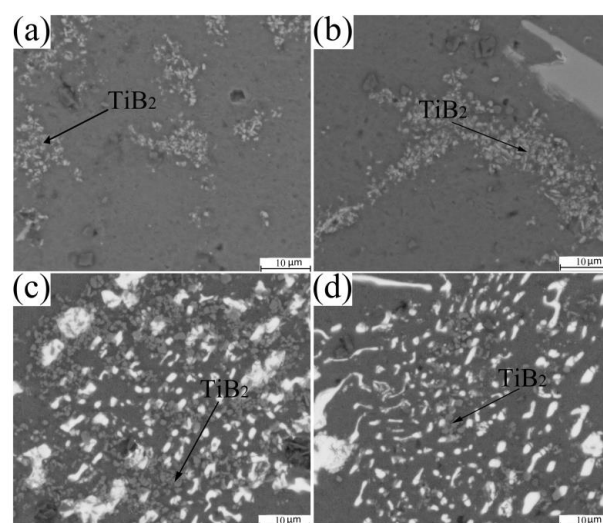


Figure 5. SEM morphologies of TiB_2 in (a) Al-5Ti-1B, (b) Al-5Ti-1B-1Ce, (c) Al-5Ti-1B-5Ce, (d) Al-5Ti-1B-10Ce.

3.2. Effect of Al-5Ti-1B-xCe Refiner on Phase Composition, Grain Size, and Microstructure of As-Cast Al-5Mg-3Zn-1Cu Alloys

Figure 6 shows the XRD patterns of the as-cast Al-5Mg-3Zn-1Cu. It can be seen that the as-cast Al-5Mg-3Zn-1Cu alloys are mainly composed of α -Al and $\text{Mg}_{32}(\text{AlCuZn})_{49}$.

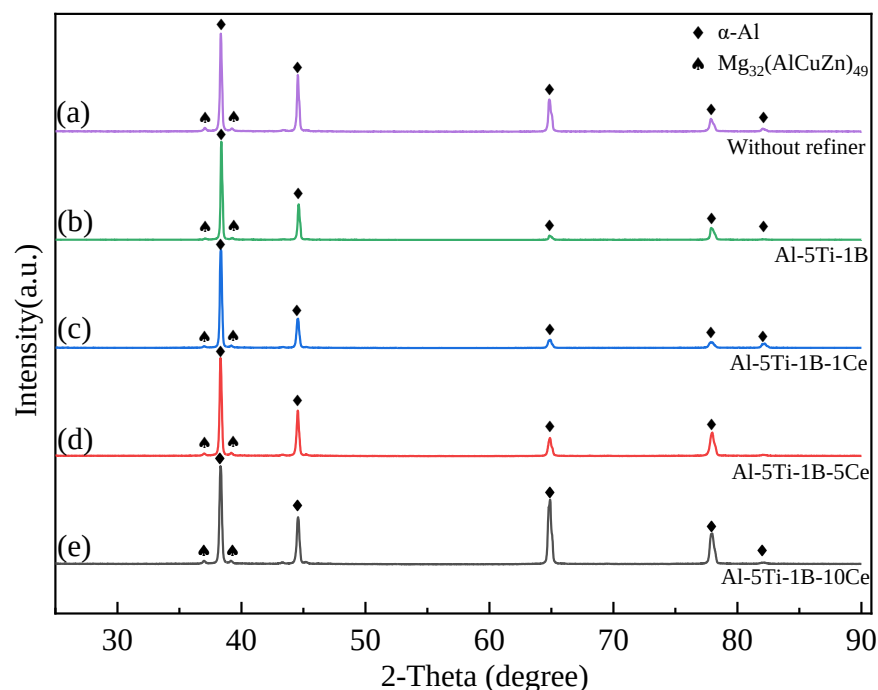


Figure 6. XRD patterns of the as-cast Al-5Mg-3Zn-1Cu alloys refined by (a) without refiner (b) Al-5Ti-1B, (c) Al-5Ti-1B-1Ce, (d) Al-5Ti-1B-5Ce, (e) Al-5Ti-1B-10Ce.

Figure 7(a1–e1) show the anode-coated optical microstructure of as-cast Al-5Mg-3Zn-1Cu alloys. Figure 7(a2–e2) show the optical microstructure of as-cast Al-5Mg-3Zn-1Cu alloys with and without refiner. Figure 7f shows the grain size of as-cast Al-5Mg-3Zn-1Cu. It can be seen from Figure 7(a1) that as-cast Al-5Mg-3Zn-1Cu alloys without a refiner lack sufficient nucleation sites during solidification, resulting in coarse α -Al dendrites and a $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase distributed along grain boundaries, with an average grain diameter of about 219.4 μm . There are many granular TiB_2 phases in the Al-5Ti-1B refiner, and the granular TiB_2 phase can serve as the heterogeneous nucleation site of α -Al, thus refining the grains of Al alloy [22,23]. When the as-cast Al-5Mg-3Zn-1Cu alloys are refined by the Al-5Ti-1B refiner, the grain diameter decreases to 84 μm , and the microstructure of the alloy changes from coarse dendrites to fine dendrites, as shown in Figure 7(b1,b2). It can be seen from Figure 7(c1,c2) that the grain size of Al-5Mg-3Zn-Cu alloy refined by the Al-5Ti-1B-1Ce refiner reduces to 47.9 μm , and the grain morphology changes from dendrites to equiaxed grain. What can be seen from Figure 7(d1,e1) is that the grain size of as-cast Al-5Mg-3Zn-1Cu alloys increased to 78.2 μm and 84.5 μm after being refined by the Al-5Ti-1B-5Ce refiner and Al-5Ti-1B-10Ce refiner, respectively.

Figure 7f shows that the Al-5Ti-1B-1Ce refiner has the best refining effect on Al-5Mg-3Zn-Cu alloy, which is due to the $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase and α -Al are both face-centered cubic, and there are eighth crystal indices between them and the mismatch is very low. According to the Bramfitt nucleation theory, the $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase can be used as the core of the heterogeneous nucleation of α -Al [27,32]. The decomposition temperature of the $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase is higher, and the phase density of $\text{Ti}_2\text{Al}_{20}\text{RE}$ (about 3.22 g/cm^3) is close to that of Al (about 2.70 g/cm^3), which is not easy to sink, so the $\text{Ti}_2\text{Al}_{20}\text{RE}$ phase can maintain the refining effect for a long time [33]. In addition, there is a layer of Ce atoms on

the TiAl_3 phase surface of the Al-5Ti-1B-1Ce refiner. Song [34] et al. found that Ce doping at the interface of TiAl_3 // Al reduces interface energy, which shows that Ce can enhance the nucleation ability of Al on the TiAl_3 surface. Furthermore, the TiB_2 particle size in Al-5Ti-1B-1Ce is small, and it can also be used as the heterogeneous nucleation site of α -Al. Therefore, the Al-5Ti-1B-1Ce refiner has an excellent refining effect and the refining effect of the Al-5Ti-1B-1Ce refiner is 43.0% higher than that of the Al-5Ti-1B refiner.

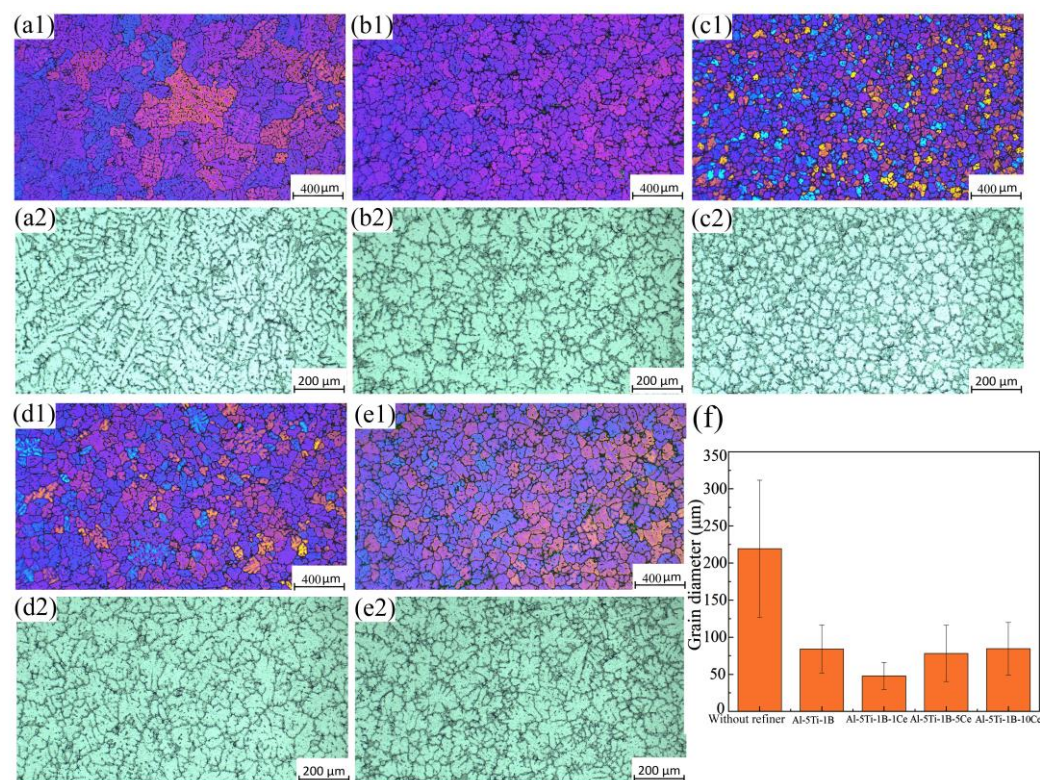


Figure 7. Microstructure of the as-cast Al-5Mg-3Zn-1Cu alloys refined by (a1,a2) without refiner (b1,b2) Al-5Ti-1B, (c1,c2) Al-5Ti-1B-1Ce, (d1,d2) Al-5Ti-1B-5Ce, (e1,e2) Al-5Ti-1B-10Ce. (f) Grain size of the as-cast Al-5Mg-3Zn-1Cu alloys before and after grain refining.

The refining effect of the Al-5Ti-1B-5Ce refiner and the Al-5Ti-1B-10Ce refiner decreased by 63.3% and 76.4% respectively compared with the Al-5Ti-1B-1Ce refiner. With the increase in Ce content in Al-5Ti-1B-xCe, the size of TiB_2 increases, and the number of TiB_2 particles decreases, so the number of sites that TiB_2 particles can provide non-uniform nucleation decreases, so the refining effects of the Al-5Ti-1B-5Ce refiner and the Al-5Ti-1B-10Ce refiner are reduced. Moreover, there are a large number of meshed Al_4Ce phases in the Al-5Ti-1B-5Ce refiner and the Al-5Ti-1B-10Ce refiner, and the occurrence of Al_4Ce with grid structure would impede the refining effect of the grain [27]. Therefore, the refining effect of the Al-5Ti-1B-5Ce refiner and the Al-5Ti-1B-10Ce refiner decreased compared with the Al-5Ti-1B-1Ce refiner.

Figure 8a–e show the SEM morphologies of the as-cast Al-5Mg-3Zn-1Cu alloys with and without refiner. Table 3 shows the element composition of Figure 8. Combined with XRD results, it can be seen that Figure 8(a1–e1) are α -Al matrix and a2–e2 are $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phases. Figure 8f shows the area proportion of the $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase and the dendrites width of the $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase of Figure 8a–e. The area proportion and dendrites width of the $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase in as-cast Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B-1Ce refiner, Al-5Ti-1B-5Ce refiner, and Al-5Ti-1B-10Ce refiner are smaller than refined by the Al-5Ti-1B refiner, which indicates that the Al-5Ti-1B-xCe refiner can reduce the dendrite size during solidification of as-cast Al-5Mg-3Zn-1Cu alloys.

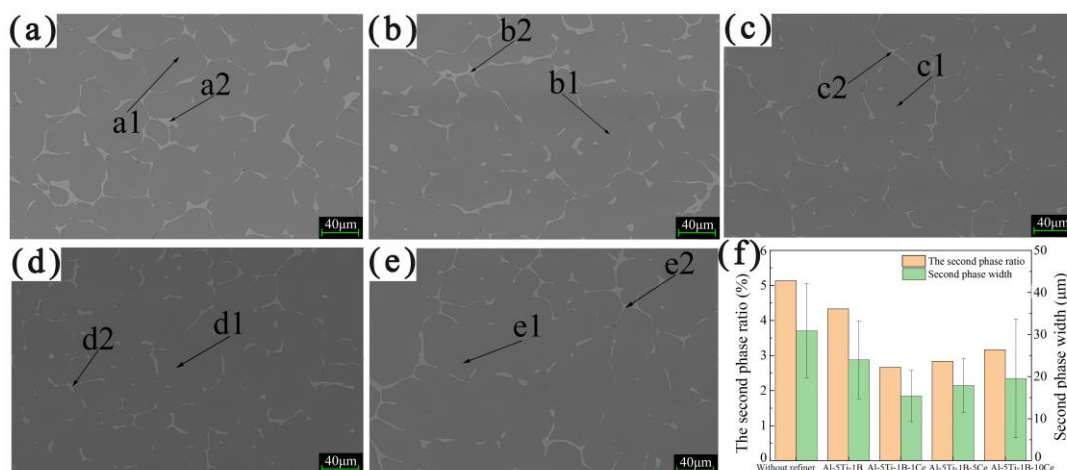


Figure 8. SEM morphologies of the as-cast Al-5Mg-3Zn-1Cu alloys refined by (a) without refiner (b) Al-5Ti-1B, (c) Al-5Ti-1B-1Ce, (d) Al-5Ti-1B-5Ce, (e) Al-5Ti-1B-10Ce. (f) Area proportion of the second phase and dendrites width of the second phase in as-cast Al-5Mg-3Zn-1Cu alloys before and after grain refining.

Table 3. EDS analysis results of the as-cast Al-5Mg-3Zn-1Cu alloys.

Refiner in Alloys	EDS Position	Elements (at.%)			
		Al	Mg	Zn	Cu
Without refiner	a1	95.29	3.56	0.97	0.18
	a2	58.91	27.15	8.74	5.20
Al-5Ti-1B	b1	93.10	5.44	1.24	0.22
	b2	61.98	25.49	7.84	4.69
Al-5Ti-1B-1Ce	c1	93.49	5.20	1.13	0.18
	c2	64.03	22.87	7.95	5.00
Al-5Ti-1B-5Ce	d1	93.14	5.44	1.18	0.24
	d2	50.12	33.99	9.69	6.12
Al-5Ti-1B-10Ce	d1	94.50	4.24	1.10	0.16
	d2	58.21	27.21	9.26	5.32

This is because the atomic radius and relative atomic mass of Ce are much larger than that of aluminum atoms, so the solubility of Ce atoms in α -Al is very low. Consequently, when Ce atoms are situated at the forefront of the solidification interface (the tip of dendrite growth), they act as impediments to growth. The diffusion and exchange of solutes are hindered, leading to a reduction in composition supercooling and ultimately decreasing the growth rates of secondary dendrites [35,36]. Therefore, the Al-Ti-B-xCe refiner can reduce the dendrite size of as-cast Al-5Mg-3Zn-1Cu alloys.

3.3. Effect of Al-5Ti-1B-xCe Refiner on Microstructure and Mechanical Properties of Solid Solution Al-5Mg-3Zn-1Cu Alloys

Figure 9 shows the SEM microstructure of the solid solution Al-5Mg-3Zn-1Cu alloys with and without refiner. According to the EDS results in Table 4, point a1-e1 are α -Al matrix. The phase in the red circle has a high Fe element content, indicating that point a2-e2 are Fe-rich intermetallic phase. The crucible used in the smelting process is an iron crucible, so it is easy to introduce Fe elements in the smelting process, and the aluminum and intermediate alloys used in the smelting also have Fe elements, so there are some Fe elements in the Al-5Mg-3Zn-1Cu alloys. According to the results of component detection, the content of Fe elements in Al-5Mg-3Zn-1Cu alloys without refiner, refined by Al-5Ti-1B, refined by Al-5Ti-1B-1Ce, refined by Al-5Ti-1B-5Ce, and refined by Al-5Ti-1B-10Ce are

0.083 wt.%, 0.089 wt.%, 0.076 wt.%, 0.076 wt.%, and 0.073 wt.%, respectively. The element composition of point a3-e3 are close to $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase in Figure 8, so it can be seen that the point a3-e3 are $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase. The Cu element in the point-like phase at points (a4) and (b4) is high, indicating that the point-like phase is a Cu-rich intermetallic phase. However, the Cu and Ce elements in the point-like phase at points (c4), (d4), and (e4) are high, indicating that the point-like phase is a Cu- and Ce-rich intermetallic phase. The number of particle phases at the grain boundary in Figure 9c–e increases with the increases in Ce content of the Al-5Ti-1B-xCe refiner. The phase in the blue circle in Figure 9e point e5 is composed of Al, Cu, and Ce, and the content of Ce and Cu is much higher than the matrix of the alloy.

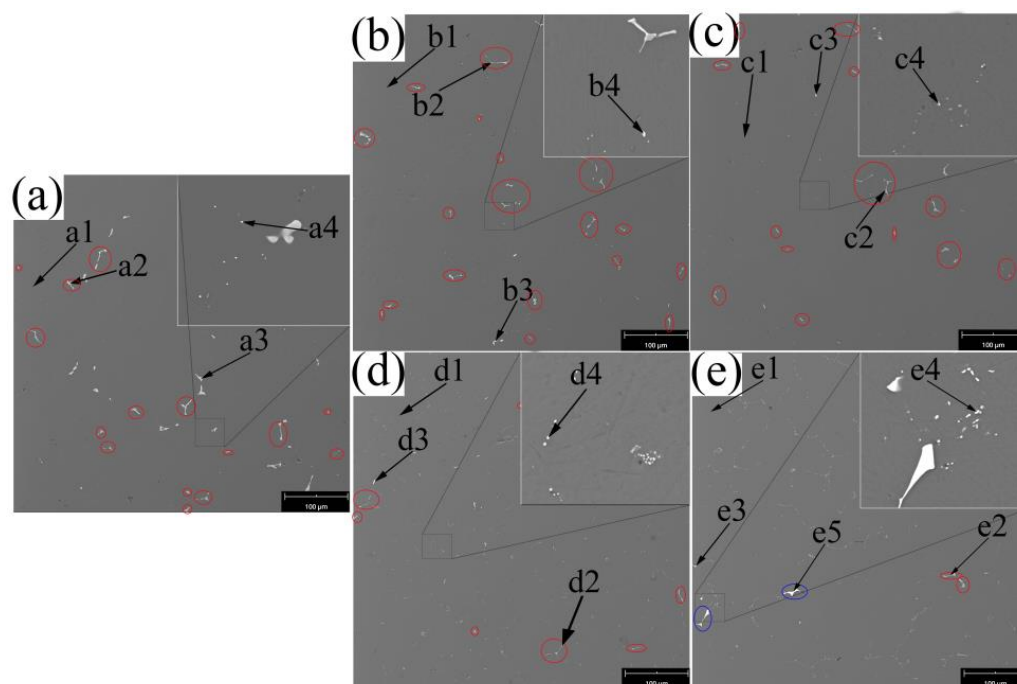


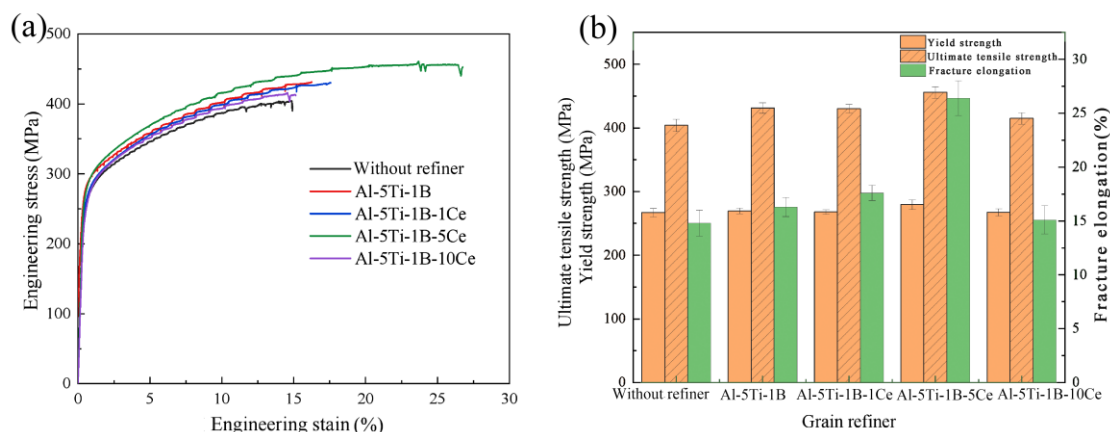
Figure 9. SEM morphologies of the solid solution Al-5Mg-3Zn-1Cu alloys refined by (a) without refiner (b) Al-5Ti-1B, (c) Al-5Ti-1B-1Ce, (d) Al-5Ti-1B-5Ce, (e) Al-5Ti-1B-10Ce.

It can be seen from the figure that the Fe-rich intermetallic phase size in Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B-1Ce refiner, Al-5Ti-1B-5Ce refiner, and Al-5Ti-1B-10Ce refiner are smaller than Al-5Mg-3Zn-1Cu alloys without refiner and refined by Al-5Ti-1B, which indicates that the Al-5Ti-1B-xCe refiner can purify the melt and reduce the size of the Fe-rich intermetallic phase in the alloy. With the increase in Ce content of the Al-5Ti-1B-xCe refiner, the size of the Fe-rich intermetallic phase in the refined Al-5Mg-3Zn-1Cu alloys gradually decreases, which is because rare-earth elements can purify the aluminum alloy melt and reduce the size of the Fe-rich intermetallic phase in the alloy [37–39].

Figure 10 shows the tensile results of the solid solution Al-5Mg-3Zn-1Cu alloys with and without refiner. Table 5 summarizes their yield strength, ultimate tensile strength, and fracture elongation. The tensile test results show that the solid solution Al-5Mg-3Zn-1Cu alloys have good plasticity, and its fracture elongation is over 14%. Refining grain is conducive to the improvement in alloy strength [40], so the strength of solid solution Al-5Mg-3Zn-1Cu alloys without refiner, refined by the Al-5Ti-1B refiner and the Al-5Ti-1B-1Ce refiner gradually increase.

Table 4. EDS analysis results of the solid solution Al-5Mg-3Zn-1Cu alloys.

Refiner in Alloys	EDS Position	Elements (at.%)					
		Al	Mg	Zn	Cu	Fe	Ce
Without refiner	a1	92.57	6.12	1.31	-	-	-
	a2	80.44	-	-	3.75	15.81	-
	a3	44.71	34.65	9.86	10.78	-	-
	a4	86.97	6.07	1.55	5.41	-	-
Al-5Ti-1B	b1	92.82	5.82	1.36	-	-	-
	b2	80.74	-	-	3.34	15.93	-
	b3	51.16	29.47	10.56	8.81	-	-
	b4	84.92	5.46	1.98	7.64	-	-
Al-5Ti-1B-1Ce	c1	92.51	6.1	1.39	-	-	-
	c2	80.87	-	-	3.48	15.64	-
	c3	44.56	33.43	10.50	11.50	-	-
	c4	83.86	5.4	1.88	7.76	-	1.1
Al-5Ti-1B-5Ce	d1	91.8	6.58	1.61	-	-	-
	d2	79.67	-	-	3.39	16.94	-
	d3	50.83	31.89	8.39	8.88	-	-
	d4	84.95	5.20	2.02	6.62	-	1.20
Al-5Ti-1B-10Ce	e1	92.72	6.04	1.23	-	-	-
	e2	80.34	-	-	3.64	16.01	-
	e3	45.80	34.83	9.50	9.68	-	-
	e4	85.71	5.36	1.74	6.17	-	1.03
	e5	66.16	-	-	27.19	0.94	5.70

**Figure 10.** Tensile property of the solid solution Al-5Mg-3Zn-1Cu alloys: (a) Engineering stress-strain curves and (b) the ultimate tensile strength, yield strength, and fracture elongation from the tensile curve.**Table 5.** Yield strength, ultimate tensile strength, and fracture elongation of the solid solution Al-5Mg-3Zn-1Cu alloys refined by different refiners.

Grain Refiner	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Fracture Elongation (%)
Without refiner	267 ± 6.6	404 ± 9.7	14.8 ± 1.20
Al-5Ti-1B	269 ± 4.3	431 ± 8.4	16.3 ± 0.90
Al-5Ti-1B-1Ce	268 ± 3.7	434 ± 6.7	17.6 ± 0.70
Al-5Ti-1B-5Ce	280 ± 7.5	456 ± 9.1	26.4 ± 1.60
Al-5Ti-1B-11Ce	268 ± 5.6	415 ± 8.9	15.1 ± 1.30

The size of the acicular Fe-rich intermetallic phase in the microstructure of solid solution Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B-5Ce refiner is greatly decreased, and the presence of coarse Fe-rich intermetallic phase reduces the strength and ductility of the alloy [41–43]. This reduction in the acicular brittle Fe-rich intermetallic phase is responsible for the increase in strength and elongation. In addition, the strength increase in the Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner is also contributed by precipitation strengthening. Precipitations in the matrix can improve the strength of the alloy [44,45]. A large number of granular Ce-rich phases are formed in solid solution Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner, which can serve as precipitation strengthening. As a result, the strength and fracture elongation of the Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner is significantly increased, reaching 456MPa and 26.4%, respectively.

It has been reported that large RE-rich phases in the aluminum alloy can cut the matrix during the process of grain deformation, thus reducing the mechanical properties of the alloy [46–48]. After being refined by Al-5Ti-1B-10Ce, the microstructure of solid solution Al-5Mg-3Zn-1Cu alloys contains a large acicular Ce-rich phase, and the Ce-rich-phase particles at the grain boundaries are connected into a network, both of which will reduce the grain boundary strength of the alloy. Therefore, solid solution Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B-11Ce have poor ductility and strength.

Figure 11 shows the fracture morphology of the solid solution Al-5Mg-3Zn-1Cu alloys. A large number of river patterns, dimples, and tear ridges can be observed at the fracture morphology of the solid solution Al-5Mg-3Zn-1Cu alloys with and without refiner, indicating that a large number of plastic deformations occurred before the fracture, which further indicates that the alloy has good plasticity.

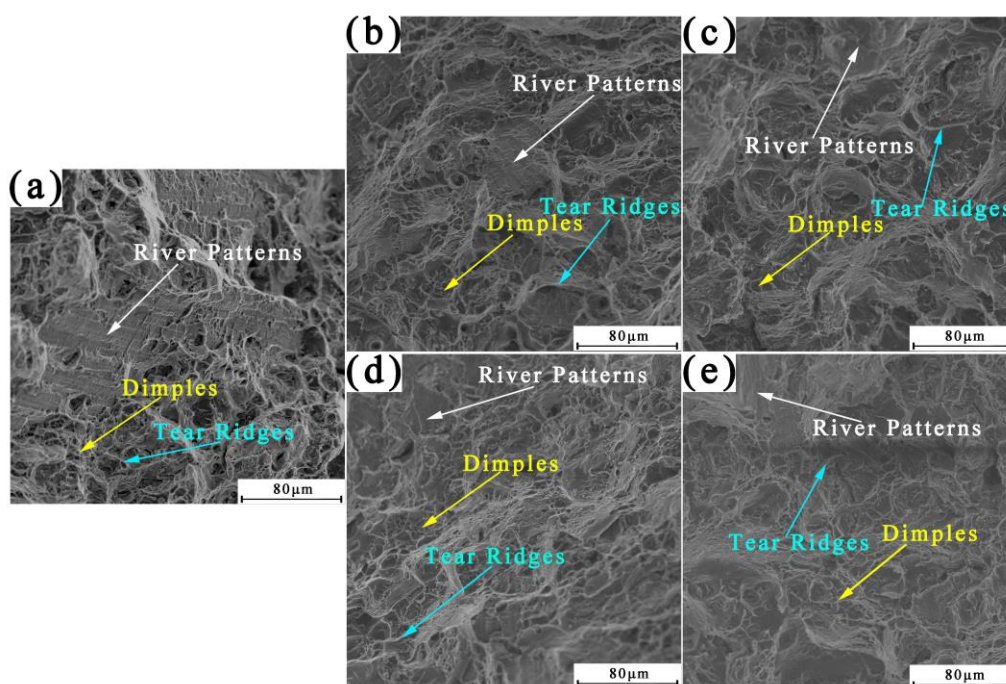


Figure 11. Fracture morphology of the solid solution Al-5Mg-3Zn-1Cu alloys refined by (a) without refiner (b) Al-5Ti-1B, (c) Al-5Ti-1B-1Ce, (d) Al-5Ti-1B-5Ce, (e) Al-5Ti-1B-10Ce.

3.4. Effect of Al-5Ti-1B-*x*Ce Refiner on Microstructure and Mechanical Properties of Aged Al-5Mg-3Zn-1Cu Alloys

According to the EDS results in Table 6, point a1-e1 are α -Al matrix. And Fe content in points a2, b2, and c2 is higher, indicating that they are Fe-rich intermetallic phases. The

Fe-rich intermetallic phase in Figure 12a,b is significantly larger than that in Figure 12c; furthermore, a smaller Fe-rich intermetallic phase is observed in Figure 12d,e. Rare-earth elements have a good purification effect on Al alloys. They can reduce the gas and non-metallic inclusions in aluminum alloy melt, and they can change the shape of the Fe-rich intermetallic phase and reduce the size of the Fe-rich intermetallic phase [49–51]. Consequently, the size of the Fe-rich intermetallic phase in aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-xCe refiner is reduced and with the increase in Ce content of the Al-5Ti-1B-xCe refiner, the size of the Fe-rich intermetallic phase in aged Al-5Mg-3Zn-1Cu alloys can be further reduced.

Table 6. EDS analysis results of the aged Al-5Mg-3Zn-1Cu alloys.

Refiner in Alloys	EDS Position	Elements (at.%)					
		Al	Mg	Zn	Cu	Fe	Ce
Without refiner	a1	92.38	6.10	1.52	-	-	-
	a2	81.03	3.24	-	3.65	12.09	-
	a3	44.67	33.70	11.20	10.43	-	-
	a4	89.75	6.86	1.38	2.02	-	-
Al-5Ti-1B	b1	92.47	6.18	1.36	-	-	-
	b2	83.15	3.24	-	2.28	11.33	-
	b3	44.67	33.70	11.20	10.43	-	-
	b4	89.75	6.86	1.38	2.02	-	-
Al-5Ti-1B-1Ce	c1	92.40	6.01	1.59	-	-	-
	c2	81.99	3.20	-	2.52	12.29	-
	c3	46.02	33.15	10.77	10.07	-	-
	c4	90.83	5.97	1.53	1.67	-	1.1
Al-5Ti-1B-5Ce	d1	92.12	6.14	1.74	-	-	-
	d2	82.23	4.42	2.21	9.48	-	1.66
Al-5Ti-1B-10Ce	e1	92.51	6.17	1.33	-	-	-
	e2	84.20	5.24	1.77	7.45	-	1.34
	e3	50.90	28.54	10.37	10.07	10.07	0.12
	e4	69.45	-	-	25.10	-	5.34

The element composition of point a3, b3, c3 and e3 are close to $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase in Figure 8, so it can be seen that the point a3, b3, c3 and e3 are $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase. The EDS results of points a4 and b4 show that the Cu content is higher, indicating that it is a Cu-rich phase. The EDS results of points c4, d2, and e2 show that the Cu and Ce contents are higher, indicating that they are rich in Ce and Cu phases. With the increase in Ce content of the Al-5Ti-1B-xCe refiner, the granular-rich Ce and Cu phases in the grain boundaries of the refined and aged Al-5Mg-3Zn-1Cu alloys increased. The EDS results of points e4 show that the Cu and Ce element content is even higher, indicating that it is a Cu- and Ce-rich phase. When the aged Al-5Mg-3Zn-1Cu alloys were refined by the Al-5Ti-1B-10Ce refiner, not only were a large number of granular Ce-rich phases formed but so were large Chinese-character Ce-rich phases.

Figure 13 shows the dark-field TEM image of the aged Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B and Al-5Ti-1B-5Ce. In the TEM image, there are many nanoscale precipitates in the aging Al-5Mg-3Zn-1Cu alloys. Combined with previous studies [17,18], it can be seen that these precipitates are semi-coherent metastable T' phases with the matrix, and the diffraction pattern of the precipitates can be clearly seen from the SAED image. The nanoscale precipitated phase of Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B-5Ce is obviously smaller than that of Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B, indicating that trace Ce element in the alloy can inhibit the growth of T' phase.

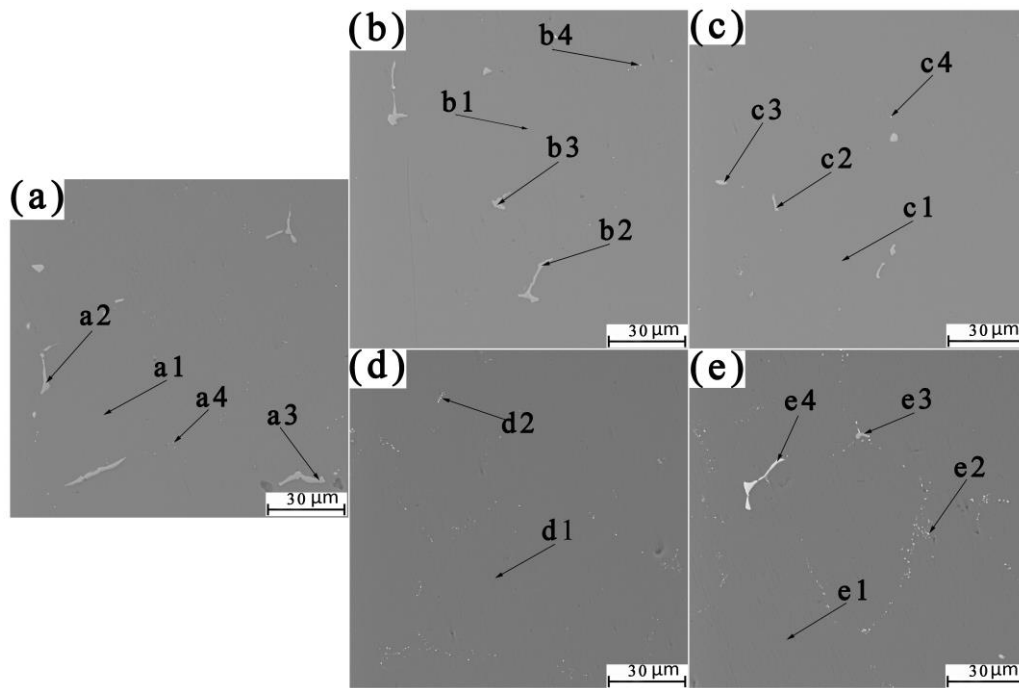


Figure 12. SEM morphologies of the aged Al-5Mg-3Zn-1Cu alloys refined by (a) without refiner (b) Al-5Ti-1B, (c) Al-5Ti-1B-1Ce, (d) Al-5Ti-1B-5Ce, (e) Al-5Ti-1B-10Ce.

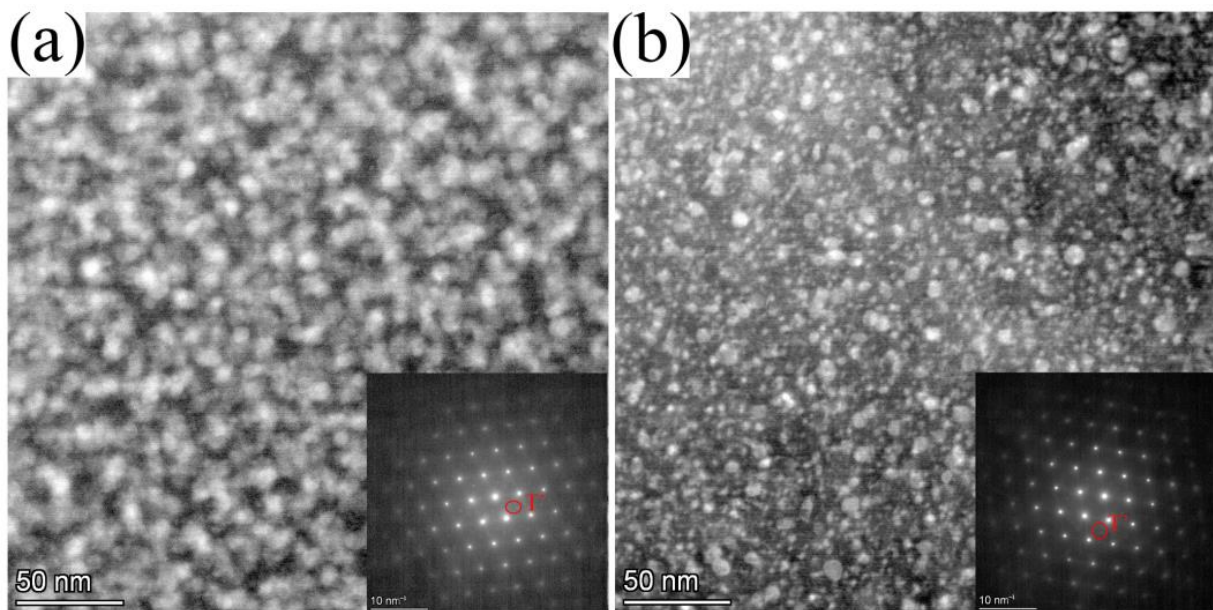


Figure 13. Dark-field TEM images of the aged Al-5Mg-3Zn-1Cu alloys refined by (a) Al-5Ti-1B, (b) Al-5Ti-1B-5Ce.

Figure 14a shows the tensile curves of the aged Al-5Mg-3Zn-1Cu alloys. Figure 14b summarizes the yield strength, ultimate tensile strength, and fracture elongation obtained from the tensile curve in Figure 14a. Table 7 shows the yield strength, ultimate tensile strength, and fracture elongation of the aged Al-5Mg-3Zn-1Cu alloys. The tensile test results show that the strength of aged Al-5Mg-3Zn-1Cu alloys increases obviously compared with the solid solution Al-5Mg-3Zn-1Cu alloys, while the ductility decreases. Al-5Mg-3Zn-1Cu alloy is composed of precipitation-strengthening alloys, and the strength of the alloys is enhanced by the precipitation of a nanoscale T' phase during aging.

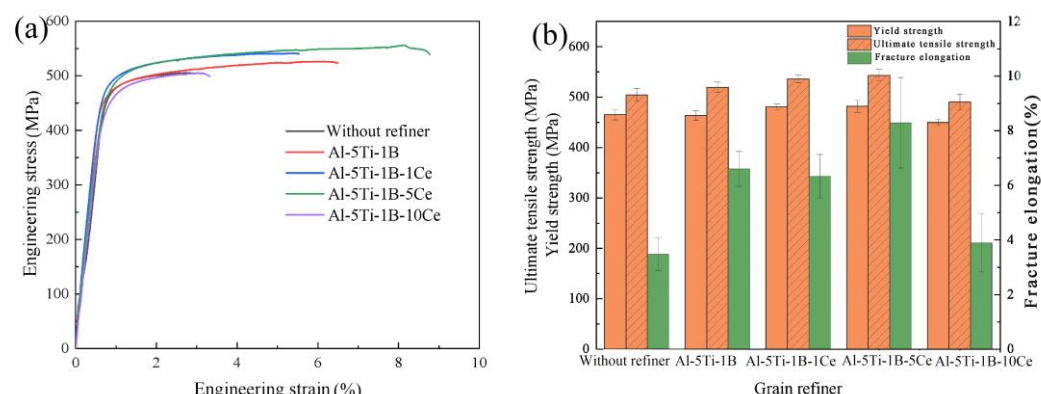


Figure 14. Tensile properties of the aged Al-5Mg-3Zn-1Cu alloys: (a) Engineering stress–strain curves and (b) the ultimate tensile strength, yield strength, and fracture elongation from the tensile curve.

Table 7. Yield strength, ultimate tensile strength, and fracture elongation of the aged Al-5Mg-3Zn-1Cu alloys.

Grain Refiner	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Fracture Elongation (%)
Without refiner	465 ± 10.5	505 ± 13.2	3.4 ± 0.60
Al-5Ti-1B	463 ± 9.4	519 ± 10.2	6.6 ± 0.60
Al-5Ti-1B-1Ce	481 ± 6.0	536 ± 7.7	6.3 ± 0.80
Al-5Ti-1B-5Ce	482 ± 11.5	543 ± 11.5	8.2 ± 1.60
Al-5Ti-1B-10Ce	450 ± 6.3	491 ± 15.2	3.8 ± 1.00

If the grain size is refined, the area of grain boundaries will increase. As a result, the great resistance to dislocation motion means the high strength of the alloy [40,52]. The grain size of Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner is smaller than Al-5Mg-3Zn-1Cu alloys without refiner, so the ultimate tensile strength of the aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner is increased by 2.9% (from 505 MPa to 519 MPa).

The acicular Fe-rich intermetallic phase in aluminum alloy reduces the mechanical properties of the alloy, and the addition of rare-earth elements can purify the aluminum alloy melt and reduce the size of the Fe-rich intermetallic phase [53–55]. The size of the Fe-rich intermetallic phase and grain size of Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-1Ce refiner are smaller than that of Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner. Therefore, the strength of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-1Ce refiner is 3.2% (from 519 MPa to 536 MPa) higher than that of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner.

A large number of granular Ce-rich phases are found at the grain boundary of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner, which can resist the movement of dislocation and improve the mechanical properties of the alloy through precipitation strengthening [44,45,56]. As can be seen from the size of the precipitated T' phase in Figure 13, the precipitated phase size of Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1b-5Ce refiner is significantly smaller than that of Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner. According to the Orowan strengthening mechanism [45,56], decreasing the size of the precipitated phase and increasing the amount of the precipitated phase can improve the strength of the alloy. Therefore, the ultimate tensile strength of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner is further increased by 4.6% (from 519 MPa to 543 MPa), compared with aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner.

With the addition of a refiner and the increase in the Ce content of the refiner, the size of the Fe-rich intermetallic phase formed in the microstructure of aged Al-5Mg-3Zn-1Cu

alloys is reduced. Because the large brittle Fe intermetallic phase is detrimental to material strength and elongation, it is believed that this reduction is the main contributor to an elongation increase, from 3.4% to 6.6 and 6.3% and then to 8.2%.

It has been known that the coarse acicular rare-earth phase and the continuous distribution of granular phase (network) in aluminum alloy reduce the boundary strength of aluminum alloy and subsequently reduce the mechanical properties of the alloy [49,57,58]. Aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-10Ce refiner have a large size acicular Ce-rich phase in the structure, and a large number of granular Ce-rich phases in the structure are connected in a network, so its mechanical properties are poor with its ultimate tensile strength and fracture elongation as 490.7 MPa and 3.8%, respectively.

Figure 15 shows the fracture morphology of aged Al-5Mg-3Zn-1Cu alloys. Figure 15a shows the fracture morphology of aged Al-5Mg-3Zn-1Cu alloys without refiner, from which a large number of intergranular cracks and cleavage planes can be observed, indicating that the fracture is a brittle fracture. Dimples, cleavage planes, and a small number of intergranular cracks can be observed in the fracture morphology of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner and the Al-5Ti-1B-1Ce refiner, indicating that the ductility of the alloy is improved.

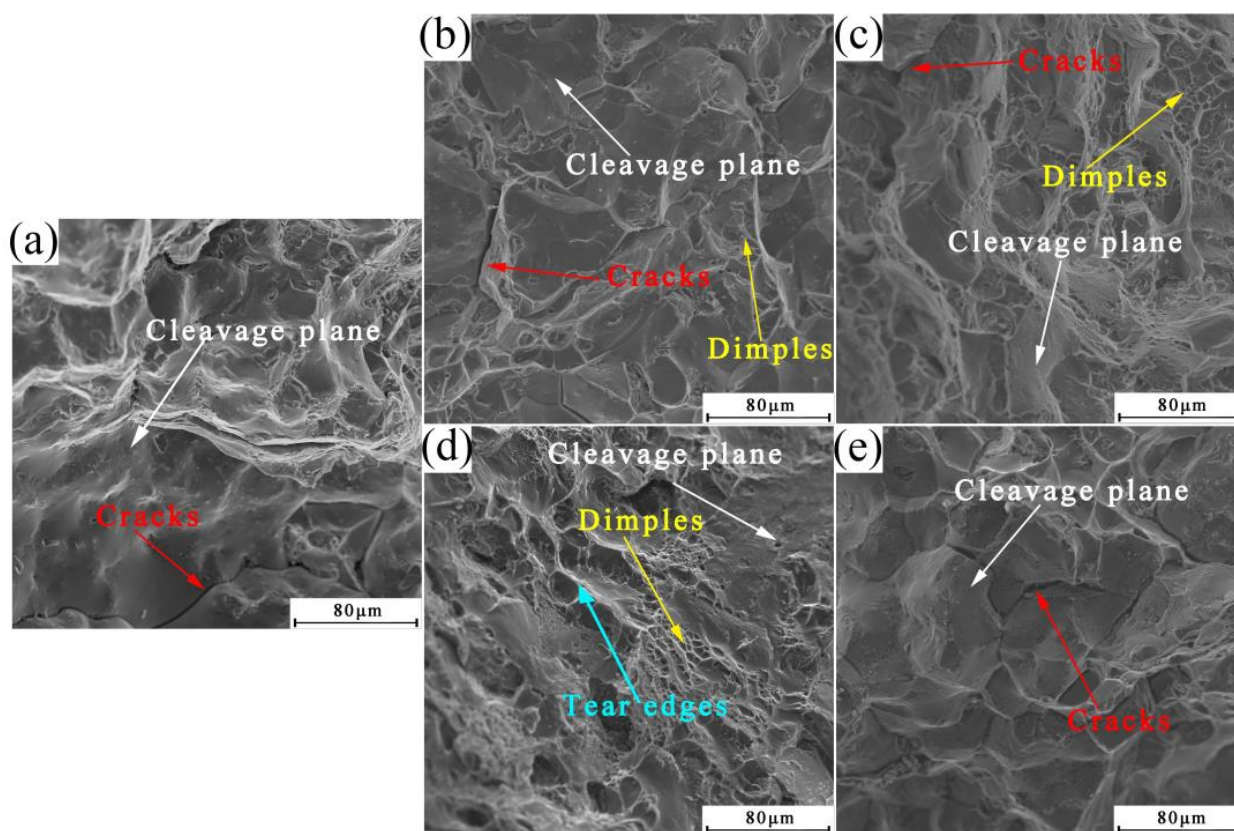


Figure 15. Fracture scanning morphology of the aged Al-5Mg-3Zn-1Cu alloys refined by (a) without refiner (b) Al-5Ti-1B, (c) Al-5Ti-1B-1Ce, (d) Al-5Ti-1B-5Ce, (e) Al-5Ti-1B-10Ce.

Figure 15d shows the fracture morphology of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner. Dimples, tear edges, and cleavage planes can be observed from the fracture morphology, indicating that the fracture is a mixture of ductile fracture and brittle fracture. Figure 15e shows the fracture morphology of aged Al-5Mg-3Zn-1Cu alloys refined by Al-5Ti-1B-10Ce. A large number of intergranular cracks and cleavage planes are observed at the fracture, indicating that the alloy fracture is mainly a brittle fracture.

4. Conclusions

In this paper, the effects of Ce content on the microstructure of Al-5Ti-1B and the effects of different refiners on the grain size, microstructure, and mechanical properties of Al-5Mg-3Zn-1Cu were studied.

- 1 The phase composition and morphology of Al-5Ti-1B will change with the increase in Ce content. When 1% Ce is added to Al-5Ti-1B, the large TiAl_3 phase changes to a fine strip-like phase, and the large $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase is formed. As the Ce content of Al-5Ti-1B increases to 5%, the plate-like TiAl_3 phase is surrounded by the $\text{Ti}_2\text{Al}_{20}\text{Ce}$ phase, and the size of the TiAl_3 phase increases. In addition, a network distribution of the Al_4Ce phase is formed in Al-5Ti-1B-5Ce and its size increased, and a network distribution of the Al_4Ce phase was formed in the microstructure. As the Ce content of Al-5Ti-1B further increased to 10%, the size and quantity of the Al_4Ce phase distributed in the microstructure increased.
- 2 The refining effect of the Al-5Ti-1B-1Ce refiner is better than the Al-5Ti-1B refiner. The grain size of as-cast Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-1Ce refiner is decreased by 43.0% compared with as-cast Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner.
- 3 Solid solution Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner have the best mechanical properties. The yield strength, ultimate tensile strength, and fracture elongation of solid solution Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner are increased by 3.79%, 5.68%, and 61.96%, respectively, compared with Solid solution Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner. The yield strength, ultimate tensile strength, and fracture elongation of aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B-5Ce refiner are increased by 3.95%, 4.59%, and 25.61%, respectively, compared with aged Al-5Mg-3Zn-1Cu alloys refined by the Al-5Ti-1B refiner.
- 4 The Al-5Ti-1B-xCe refiner can reduce the size of the $\text{Mg}_{32}(\text{AlCuZn})_{49}$ phase and the Fe-rich intermetallic phase of Al-5Mg-3Zn-1Cu alloys, which could improve the casting performance of the alloy.

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