Effect of Al Content on Microstructure and Properties of Zn-Cu-Al Alloy

Hongxing Wang\textsuperscript{a,b}, Yan Zhang\textsuperscript{a,b}, Changsheng Wang\textsuperscript{b}, Shuo Cao\textsuperscript{b}, Wan Bai\textsuperscript{b}, Canhui Wu\textsuperscript{b} and Jiahao Qian\textsuperscript{b}

\textsuperscript{a}School of Materials Science and Engineering, Nanjing Institute of Technology, 1Hongjing venue, Nanjing 211167, PR China
\textsuperscript{b}Key Laboratory of Advanced Structural Materials and Application Technology of Jiangsu Province, 1Hongjing venue, Nanjing 211167, PR China
Email: wanghx@njit.edu.cn

Abstract. Zn-Cu-Al zinc alloy was prepared by metal mould casting. The effects of Al addition on the microstructure, electrical conductivity and wear resistance of Zn-Cu-Al alloy were studied. The results show that the structure of Zn-Cu-Al alloy is composed of Zn solid solution containing Cu and Al (\(\eta\) phase), eutectic phase (\(\alpha+\eta\)) and CuZn\textsubscript{5} (\(\varepsilon\) phase); Al\textsubscript{0.4}Zn\textsubscript{0.6} phase appeared when Al addition content exceeded 2.0wt.%; With the increase of Al addition content, eutectic phase (\(\alpha+\eta\)) content increased and \(\eta\) phase grain refined. Meanwhile, the hardness and electrical conductivity of the alloy increase with the increase of Al addition content. When the addition of Al is 5.0 wt.\%, the hardness and electrical conductivity of the alloy reach the maximum, 151HV and 26.4\% IACS, respectively. The wear mechanism of the alloy is mainly plastic deformation with a mixture mode of plastic deformation and adhesion.

1. Introduction

With the increasing number of fuel vehicles, a large number of vehicle exhaust emissions have aggravated the degree of environmental pollution. In recent years, new energy electric vehicles have been put into use, effectively reducing the environmental pollution caused by the exhaust emissions of fuel vehicles. With the increasing consumption of new energy electric vehicles, the demand for copper alloy parts related to new energy electric vehicles is also increasing, which increases the price of copper and its alloys and the manufacturing cost of new energy electric vehicles. Therefore, the research and development of low-cost new metal materials, partly replacing copper alloys, can reduce the dependence on copper and its alloys, and also reduce the manufacturing cost of new energy electric vehicles.

Zinc alloy is mainly used in hardware, daily decoration, building materials, automotive parts, coatings and other fields because of their characteristics of low melting point, good casting performance and easy cutting [1, 2]. Zinc alloys mainly consist of zinc-aluminium alloys and zinc-copper alloys. At present, the main focus is on the study of the structure, corrosion and strength of high aluminum zinc alloy and high copper zinc alloy [3-8], while the study of the structure and properties of low copper zinc alloy and low aluminum zinc alloy is relatively less [9, 10], especially the electrical conductivity of zinc alloy.

The addition of titanium and magnesium in zinc can refine the grain size, improve creep resistance and plasticity of the alloy. Magnesium can increase strength, but make alloy brittle [10-13]. In addition, the mechanical properties of zinc alloys are similar to that of brass by means of deformation or heat treatment, which makes zinc alloys hopeful to be substitutes for copper alloys [14, 15]. Al has high...
conductivity, which is second only to Ag, Cu and Au. In this paper, the effect of Al addition on the microstructure, wear resistance and electrical conductivity of Zn-1.25Cu alloy is studied, which provides experimental basis and theoretical support for the development of the application of zinc alloy.

2. Experimental

Pure Zn (99.9%), pure Cu (99.9%) and pure Al (99.9%) were used as raw materials. The crucible resistance furnace (model: SG2-5-10) is used as the melting equipment, and the alloy is melted in the graphite crucible. After melting, the liquid metal is poured into the Y-shaped metal casting mould to form. The smelting process of zinc alloy is as follows: firstly, pure zinc block is put into the graphite crucible in resistance furnace, at the same time, a certain amount of charcoal particles with diameter of 20 cm are added, and the melting temperature is set at 480℃. When most pure zinc is melted, copper particles with a diameter of 1 cm are added to the zinc solution, and the temperature is adjusted to 600℃ for heat preservation. After the copper is completely melted, the temperature rises to 650℃, the aluminum block is pressed into with the self-made bell jar and the alloy liquid is rotated and stirred. After the aluminum melts completely, the temperature drops to 550℃. After the slag is drawn, the molten metal is poured into the mould preheated to 150℃. It is cooled to about 100℃ and the parts are taken out. Alloy addition composition (wt.%): Cu is 1.25, Al is 1.25, 1.5, 2.0, 3.0 and 5.0, and Zn is the remainder.

Samples with size of 20 mm × 15 mm × 5 mm were machined by WEDM. The etallographic corrosive formulation of zinc alloy is (mass percentage, %): CrO_3:Na_2SO_4:H_2O=20:1.5:100. OLYMPUS GX51 metallographic microscope was used for metallographic observation and JSM-6380LV scanning electron microscopy (SEM) and energy spectrum analysis (EDS) were used to analyze the microstructure of the alloy. X-ray diffractometer (Bruker D8 Advance) was used to analyze the alloy structure, copper target, tube current is 40 mA, tube voltage is 40 kV, and scanning speed is 5 Degree/min.

The microhardness of the alloy was measured by FM700 microhardness tester. Test conditions: pressure head load 10 N, loading time 15 s, in five different parts of the test, take the average value.

Friction experiments of alloy specimens were carried out using MFT-3000 (Rtec) wear tester. GCr15 ball (φ12 mm, quenched state, hardness HRC63) is grinding ball. Test conditions: reciprocating, radius 6 mm, load 30 N, sliding speed 10 mm.s⁻¹, time 15 min, ambient temperature room temperature, dry friction.

The resistance test sample is machined into a circular rod of 2.0 mm × 60 mm by WEDM. Before the resistance test, the surface of the rod is polished with sandpaper, and the rod is measured three times in different parts, and the average value is taken. The length of the bar test resistance is fixed at 20 mm, the test position is changed for three times, and the average value is obtained. The digital DC bridge (model QJ84A) is used to measure resistance. The formula for calculating resistivity is as follows:

\[ \rho = \frac{R \times S}{L} \]  (1)

The electrical conductivity of the alloy can be obtained by formula (1) and formula (2). The formula for calculating electrical conductivity is as follows:

\[ K = \frac{0.01724}{\rho} \times 100\% \]  (2)

There is, K, conductivity, IACS; \( \rho \), sample resistivity, Ωmm²/m; R, sample resistance, Ω; S, Cross Section Area of Sample, mm²; L, the length of testing the resistance part of the sample, m.

3. Results and Discussion

3.1. Microstructure

Fig. 1 shows the metallographic structure of Zn-Cu-Al alloys with different additions of Al. It can be seen from Fig. 1 that the structure of Zn-Cu-Al alloy is mainly composed of gray-white dendrite η phase (Zn solid solution containing Cu and Al) and interdendritic black eutectic. With the increase of
Al content, the gray-white dendrites are refined and the volume fraction decreases, while the volume fraction of black eutectic increases, and the \( \eta \) phase becomes rounded. The main reason is that during solidification, on the one hand, Al distributes around primary dendrites, which prevents secondary dendrite growth of solid solution, increases the number of nuclei of primary phase, makes them distribute uniformly, and refines the grain size of primary phase; on the other hand, when the addition content of Al increases, the amount of Al in the melt is also increasing, reaching the composition near eutectic reaction, which leads to the number of eutectic phases in the solidified structure increase significantly.

Fig. 1. Optical images of Zn-Cu-Al with different addition of Al: (a) 1.25; (b) 1.5; (c) 2.0; (d) 3.0; (e) 4.0

Fig. 2 shows the SEM photos of Zn-Cu-Al alloys with different amounts of Al. It can be seen from Fig. 2 that the eutectic phase between dendrites of \( \eta \) phase in the as-cast structure of Zn-Cu-Al is layer structure, mainly consisting of \( \eta \) phase and \( \alpha \) phase (Al-rich phase) [10, 15]. The number of eutectic structure increases significantly with the increase of Al addition. The positions of "1", "2" and "3" in Fig. 2 are analyzed by elemental energy spectrum. The results are shown in Table 1. From Table 1, it can be seen that when the content of Cu is 1.25wt.% and the content of Al is 1.25-5.0wt.%, the content range of elements in the bid "1" in Figure 2 is: Al 1.27-1.82wt.%, Cu 1.75-2.61wt.%, Zn 95.31-96.88wt.%, and the structure of the site 1 is a Zn solid solution phase (\( \eta \) phase)containing solute atoms, Cu and Al; the content range of elements in the bid "2" is: Al 12.24-21.36wt.%, Cu 1.5%. 8-2.08wt% and Zn 77.05 - 85.67wt%. The structure of the site 2 is eutectic structure consisting of \( \eta \) phase and \( \alpha \) phase (Al-rich phase).
Figure 2. SEM images of Zn-Cu-Al alloy (wt.%): (a) 1.25; (b) 1.5; (c) 2.0; (d) 3.0; (e) 5.0

Table 1. Energy spectrum analysis of cast microstructure of Zn-Cu-Al alloy in different locations shown in Fig. 2 (wt.%)

| Positions | Elements (wt.%) |
|-----------|----------------|
|           | Cu  | Al  | Zn  |
| a1        | 2.87| 1.82| 95.31 |
| a2        | 1.76| 18.04| 80.20 |
| b1        | 2.61| 1.49| 95.90 |
| b2        | 1.71| 18.67| 79.62 |
| c1        | 1.85| 1.27| 96.88 |
| c2        | 1.78| 18.16| 80.05 |
| d1        | 1.75| 1.60| 96.65 |
| d2        | 1.71| 18.71| 79.58 |
| d3        | 1.91| 17.04| 81.05 |
| e1        | 1.68| 1.63| 96.69 |
| e2        | 1.70| 19.63| 78.67 |
| e3        | 1.74| 18.27| 79.99 |

Table 1 shows the results of elemental energy spectrum analysis at different locations in the structure of Zn-Cu-Al alloy. From the data in Table 2, it can be seen that with the increase of Al addition, the total content of Cu and Al in the marked "1" region decreases basically, from 4.69 wt.% when Al addition is 1.25 wt.% to 3.31 wt.% when Al addition is 5.0 wt.%, indicating that the solid
The solubility of alloy elements Cu and Al in the zinc matrix is decreasing. The atomic ratio of elements Zn and Al in the "2" region of the table is close to 3:2.

In order to further analyze the effect regularities of Al addition on the structure of Zn-Cu-Al alloy, the area at "1" in Fig. 2 is enlarged, as shown in Fig. 3. From Fig. 3, it can be seen that when Al addition content is 1.25wt.%, fine spherical particles with nano-scale are precipitated and dispersed in \( \eta \) phase; when Al addition content is 1.5wt.%, the size of spherical particles grows and the size difference between particles is not obvious; when Al addition content is 2.0wt.%, some spherical precipitated particles turn into short strips, and the size difference between particles increases obviously; when Al addition content is 3.0 wt.% and 5.0wt.%, some precipitated particles coarsen and the number of precipitated particles increases. The elemental energy spectrum analysis of the precipitated particles in \( \eta \) phase is carried out. As shown in Fig. 3 (f), the results show that the precipitated particles are composed of elements Zn, Cu and Al with atomic contents of 89.38 at.%, 3.45 at.% and 7.18 at.% respectively.

![Figure 3. Magnified SEM images of region marked by 1 in Fig. 2: (a) 1.25; (b) 1.5; (c) 2.0; (d) 3.0; (e) 5.0; (f) EDS of plus in Fig. e](image)

### 3.2. Phase Structure

Fig. 4 shows the XRD spectra of Zn-Cu-Al alloys with different Al contents. It can be seen from Fig. 1 that when the addition amount of Al is 1.25wt.% ~ 2.0wt.%, the Zn-Cu-Al alloy mainly consists of two phases: \( \eta \) phase (Zn) and \( \varepsilon \) phase (ZnCu5). Al0.4Zn0.6 phase appeared when the addition amount exceeded 3.0wt%. However, the intensity of the diffraction peak is very weak. An important factor affecting the formation of compounds between elements is the electronegativity of elements. The greater the difference of electronegativity between elements, the stronger the possibility of bonding between elements and the easier the formation of compounds. The electronegativity of Zn, Cu and...
Al is 1.65, 1.90 and 1.50 respectively. The difference of electronegativity between Zn and Al is 0.15, which is much larger than the difference between Zn and Cu (0.4). It is judged from thermodynamic theory that Zn and Cu are easy to form compounds. Previous studies [16-18] have shown that the solid solubility of Cu in Zn is only 0.3wt.% at room temperature in Zn-Cu binary alloy [19], and increases to 2.7wt.% at 425 °C. When the concentration of Cu exceeds 1 wt.% metastable phase ε (CuZn5) is formed, and the ε phase is generally dispersed in the matrix with fine particles. In this experiment, the addition content of Cu element is 1.25wt%. According to the results of energy spectrum analysis in Table 1, the concentration of copper in different regions of the alloy is more than 1wt%. It can be determined that there is ε phase in the alloy structure. In the XRD diagram of Figure 4, the characteristic peak of ε phase with weak strength appears. However, due to the small size and dispersive distribution of the ε phase, the ε phase can not be clearly observed in the SEM images of the alloy microstructures in Figs. 2 and 3.

According to the Zn-Al phase diagram [19], there are mainly η (Zn) phases, solid solution based on zinc, dense hexagonal structure; α (Al) phase, solid solution based on aluminium, face-centered cubic structure; (α + η) eutectoid phase, solid solution based on aluminium or zinc-aluminium, and the lamellar solid solution η (Zn) based on zinc. Some weaker peaks correspond to the CuZn5 phase, i.e. ε phase. Because the η phase and the ε phase have the same lattice type, hexagonal structures, and the lattice constants are very close, which leads to the coincidence of the two phases on the diffraction peaks at a specific angle. Because of the large volume fraction of η phase, the intensity of the diffraction peak is very high, and its diffraction peak masks the relatively weak peak of the ε phase.

**Figure 4.** XRD patterns of Zn-Cu-Al alloy with different Al addition content (wt.%): (a) 1.25; (b) 1.5; (c) 2.0; (d) 3.0;(e)5.0

### 3.3. Electrical Conductivity

Fig. 5 shows the effect of Al addition on the electrical conductivity of Zn-Cu-Al alloy. As can be seen from Fig. 5, the electrical conductivity of the alloy increases with the addition of Al. When the Al addition content in the alloy is 1.25, 1.5, 2.0, 3.0 and 5.0wt.% respectively, the corresponding electrical conductivity is 23.31 IACS, 23.56 IACS, 23.95IACS, 24.61 IACS% and 25.07 IACS%. Comparing to the alloy with 1.25wt.%Al addition content, the conductivity increases by 7.5% when the Al addition content is 5.0wt.%.

Generally, the electrical conductivity of alloys is lower than that of pure metals. This is because the lattice arrangement of pure metal is relatively orderly, and the electron is less hindered in the transmission process. However, after alloying, because of the difference of atomic radius between solute and solvents, the lattice shrinkage or expansion of the matrix will be caused to varying degrees by the formation of solid solution or second phase, resulting in lattice distortion, which will increase the impediment of electronic movement and decrease the conductivity of the alloy. Moreover, the scattering effect of lattice distortion caused by atoms in solid solution on the electrons in the matrix is higher than that caused by reciprocation. The scattering effect caused by the second phase is much stronger and the electrical conductivity is much lower [20, 21]. The atomic radius of Zn is 1.39 Å, that of Cu is 1.28 Å, and that of Al is 1.43 Å. Therefore, in theory, the conductivity of Zn-Cu-Al alloy
should decrease with the increase of Al addition content, but in fact, the conductivity of Zn-Cu-Al alloy increases with the increase of Al addition content.

According to the results of microstructures and EDS analysis, when the Al addition content ranges from 1.25% to 5.0wt.%, the total amount of Cu and Al in solid solution in η phase decreases with the increase of Al addition content, which is beneficial to improve the conductivity of the alloy. In addition, with the increase of Al addition content, the grain size of η phase in Zn-Cu-Al alloy decreases, and the area of grain boundary increases. Meanwhile, the particles precipitated from η phase coarsen. Both inhibit the conductivity of the alloy. From the morphology of Figs. 1 and 2, the state of η phase in Zn-Cu-Al alloy changes from continuous flaking at low Al content to discrete distribution at high Al content. On the contrary, the eutectic phase (α+η) which was originally dispersed between η phase crystals joined into pieces, and the number increased significantly. This structural change may be the main reason for the increase of electrical conductivity of the alloy.

Figure 5. Effects of Al on the electrical conductivity of Zn-Cu-Al alloy

3.4. Microhardness
Fig. 6 shows the effect of Al addition on the microhardness and friction coefficient of Zn-Cu-Al alloy. It can be seen from Fig.6 that the microhardness and friction coefficient of the alloy increase with the increase of Al addition. The hardness of the alloy increases from 99 HV at 1.25 wt.% Al addition to 125 HV at 5.0 wt.% Al addition and the corresponding friction coefficient decreases from 0.55 to 0.45. From the analysis of the microstructure of the alloy, it can be seen that the increase of the hardness of the alloy is mainly attributed to the increase of the eutectic phase amount. In addition, the alloying element Al has inoculation effect. With the increase of content, the refining effect of η phase is obvious [9]. η phase is densely arranged hexagonal crystal structure, lattice constant is a=(2.6655±0.0001) Å, c=(4.9494±0.0003) Å, α phase is face-Centered Cubic with good plasticity, lattice constant a=(4.0474±0.0002)Å, ε phase (CuZn5) belongs to hard and brittle phase with HV150 hardness and is much higher than η phase (HV83.5) [22]. During the plastic deformation of the alloy, the deformation of the ε phase (CuZn5) is not easy to occur. The eutectic phase (α+η) is layered structure and microhardness is 140 HV [23].

3.5. Wear
From the curve of friction coefficient varying with sliding time in Fig. 6(b), the fluctuation trend of friction coefficient increases with the increase of Al content in the alloy. Especially when Al addition content is 5 wt.%, the fluctuation range of friction coefficient is larger, about 0.07, while the fluctuation range of friction coefficient of other alloys is about 0.02. The fluctuation of friction coefficient reflects the number, size and distribution of hard phases in the alloy. In the friction process, the α phase acts as the main carrier, while the η phase acts as the solid lubricant [24, 25].
Figure 6. Effects of Al on the microhardness and frictional coefficient of Zn-Cu-Al alloy: (a) microhardness; (b) frictional coefficient

Fig. 7 shows the morphology of wear marks of Zn-Cu-Al with different Al additions with loads of 30N, sliding speed of 10mm/s, sliding time of 15min and dry friction. As can be seen from Fig. 7, there are two characteristic morphologies on the surface of the wear marks of the alloy: plastic deformation and peeling. When the Al addition content is 1.25–2.0wt.%, the friction bearing body is η phase with lower hardness and better plasticity. Under the forward extrusion of the grinding ball, the material in the friction zone is easy to be pushed to edges, resulting in greater plastic deformation. At the same time, under the action of shear stress, the surface material of wear marks is transferred and appears peeling or delamination. The surface of the wear marks of the alloys shows obvious plastic deformation and local material detachment. The wear mechanism is a mixture of plastic deformation and adhesive wear, and plastic deformation is dominant. When the Al addition content is 3.0wt.% and 5.0wt.%, the friction bearing body is a phase of α+η with high hardness and good plasticity. In the friction process, α phase acts as the main bearing body and the η phase acts as the solid lubricant, the stress state and lubrication state of the alloy under grinding are improved. The surface of alloy wear marks is smooth and the degree of plastic deformation decreases. The wear resistance of the alloy increases with the increase of hardness and strength [26]. The wear mechanism of the alloy is mainly plastic deformation.

Figure 7. SEM micrographs of Zn-Cu-Al alloy with different Al content (wt.%): (a) 1.25; (b) 1.5; (c) 2.0; (d) 3.0; (e) 5.0
4. Conclusions

Zn-Cu-Al zinc alloy with different content of Al was prepared by metal mould casting.

When Al addition content is 1.25wt.%~2.0wt.%, the alloy structure consists of Zn solid solution containing Cu and Al (η phase), eutectic phase (α+η) and CuZn5 (ε phase). Al0.4Zn0.6 phase appeared when Al addition exceeded 2.0wt%.

With the increase of Al content, the eutectic phase content in the alloy structure increases and the η phase grain refines. The microhardness and electrical conductivity of the alloy increase with the increase of Al content. When Al addition content is 5.0wt.%, the hardness and electrical conductivity reach the maximum, 151HV and 26.4% IACS, respectively.

When the Al addition content is less than 3.0wt.%, the wear mechanism of the alloy is a composite mechanism of plastic deformation and adhesive wear, and plastic deformation is dominant. When the Al addition content is less than 3.0wt.%, the wear mechanism of the alloy is mainly plastic deformation.

5. Acknowledgements

The project is financially supported by the Jiangsu Key Laboratory of Advanced Structural Materials and Applied Technology Open Fund (ASMA 201506 and ASMA201706); Jiangsu University Students Innovation and Entrepreneurship Training Program 201711276052X); Science and technology innovation fund for college students of Nanjing Institute of Engineering (TB20190207).

6. References

[1] Savaşkan T, Maleki R A, 2014 Tribol. T., 57 435.
[2] Tanaka T, Kushibe A, Kohzu M, Takigawa Y, Higashi K, 2008 Scripta Mater., 59 215.
[3] Yan S Q, Xie J P, Liu Z X, Wang W Y, Wang A Q, Li J W, 2010 J. Mater. Sci. Technol., 26 648.
[4] Liu T, Si N C, Liu G L, Zhang R, Qi C, 2016 Trans. Nonferrous Met. Soc. China., 26 1775.
[5] Sánchez-Martínez A, Cruz A, González-Nava M, Suárez M A, 2016 Mater. Des., 108 494.
[6] Kan T S, Azakl Z, 2008 Wear, 264 920.
[7] Bobi B, Bajat J, Aivomc-pavlovi Z, Bobi I, Jegdi B, 2013 Trans. Nonferrous Met. Soc. China., 23 931.
[8] Kaya H, Cadiirli E, Ulgen A, 2011 Mater. Des., 32 900.
[9] Liu Z L, Li R Q, Jiang R P, Li X Q, Zhang M X, 2016 J. Alloys Comp., 687 885.
[10] Wu Z. C., Sandløbes S., Wu L., Hu W. P., Gottstein G., Korte-Kerzel S., Mater. Sci. Eng. A. 651 (2016) 675-687.
[11] Du D, Guan G, Gagnoud A, Fautrelle Y, Ren Z M, Lu X, Wang G H, Dai Y M, Wang Q L, Li X, 2016 Mater. Charact., 111 31.
[12] Boczkal G, Palka P, Sułkowski B, Mikulowski B, 2017 Mater. Sci. Eng. A 690 254.
[13] Ares A E, Gassa L M, Schvezov C E, Rosenberger M R, 2012 Mater. Chem. Phys., 136 394.
[14] Savaşkan T, Hekimoğlu A P, 2014 Mater. Sci. Eng. A 603 52.
[15] Zhang Y M, Yang L J, Zeng X D, Zheng B Z, Song Z L, 2013 Mater. Des., 2013 50 223.
[16] Prasad B K, 2004 Mater. Sci. Eng. A, 367 63.
[17] Costaa E M, Costab C E, Vecchiaia F D, Ricka C, Scherera M, Santosca C A, Dedavida B A, J. Alloys Comp., 488 89.
[18] Sharififar M, Mousavi S A A A, 2014 Mater. Sci. Eng. A, 594 118.
[19] Yao C Z, Tay S L, Zhu T P, Shang H F, Gao W, 2015 J. Alloys Comp., 645 131.
[20] Ying T, Zheng M Y, Li Z T, Qiao X G, Xu S W, 2015 J. Alloys Comp., 621 250.
[21] Zhang D F, Zhao X B, Shi G L, Qi F G, 2011 Rare Metal Mat. Eng. 40 418.
[22] Ma D, Li Y, Ng S C, Jones H, 2000 Acta Mater., 48 419.
[23] Mahmudi R, Alibabaie S, 2013 Mater. Sci. Eng. A 559 421.
[24] Savaskan T, 2004 Tribol.Int., 37 45.
[25] Mojaver R, Shahverdi H R, 2010 Wear, 268 605.
[26] Savaşkan T, Maleki R A, Tan H O, 2015 Tribol. Int., 81 105.