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Effect of Al on the mechanical properties and corrosion resistance of Pb-Al alloy

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Abstract. A set of binary Pb-Al alloys with different Al contents were designed in this work. The mechanical properties and corrosion resistance of Pb-Al alloys were investigated with help of tensile test, Charpy V-notch impact test and salt spray corrosion test (SSCT). And the microstructure was observed by optical microscopy. The results showed that microstructure of all alloys were twin structure, and the twin structure was gradually refined with the increase of Al content. Al dissolved in matrix could significantly improve the tensile strength, impact energy and corrosion resistance. However, a higher content of Al would harm the mechanical properties and corrosion resistance. It may be due to the heterogeneous precipitation of Al rich phase.
Key Words: Pb-Al alloy, mechanical property, corrosion resistance, salt spray corrosion test, microstructure.

1. Introduction

Electrical equipment with porcelain bushings is the most basic electrical components in power system. However, ceramics is prone to fragility fractures due to the resonance in earthquake. The practice has proved that installing dampers can enhance the seismic capacity of electric porcelain equipment by changing the free vibration characteristic and increasing the damping[1]. Traditionally, dampers are made of rubber, but rubber is easy to ageing and its service life is short[2, 3]. Compared with rubber dampers, metal dampers have the advantages of long service life, stable performance, etc. Metal dampers are mainly made of lead or mild steel, and the plastic deformation of the metal is used to absorb the earthquake energy[4-6]. Lead has excellent toughness and plasticity at room temperature and low temperature, and can absorb a large amount of energy during the process of deformation. While lead has good plasticity, the low tensile and compressive strength limits its applications. In order to apply lead better in industry, it is necessary to improve the strength of lead. On the other hand, metal dampers are usually used in the wild field. Under the comprehensive effects of atmospheric oxygen, Cl^-, HCO_3^- and SO_4^{2-} ions in the long-term service process, lead work pieces are corroded seriously. It causes serious damage to the matrix and reduces the reliability of work pieces[7]. Therefore, it is needed to improve the corrosion resistance of lead in the natural environment on the basis of improving the strength, so as to prolong their service life.

In theory, the strength of metals can be improved by grain size strengthening, cold deformation dislocation strengthening, solid solution strengthening, aging precipitation strengthening, phase transformation strengthening, etc[8]. However, the strengthening effect of grain refinement is actually ineffective in lead due to the fact that the creep strain rate of fine-grain lead is larger than that of coarse-grain lead. Dislocation enhancement can only play a role below the recrystallization temperature. The room temperature is in the range of recovery and recrystallization temperature of lead, so it is generally unable to make use of cold deformation to strengthen the lead. Aging hardening is a strengthening way for many alloys. But the enhancing effects will gradually disappear because of the coarsening behavior of the precipitates in lead alloys[7]. Based on the above reasons, lead alloys were strengthened by solid solution strengthening in this paper. Moreover, adding a small amount of alloying elements is beneficial to the improvement of corrosion resistance[9].

The study of lead based binary alloy shows that the solid solution strengthening ratio, ds/dc(s: strength, c: concentration), increasing in order as follows: thallium, bismuth, tin, cadmium, antimony, lithium, arsenic, calcium, copper and barium[7]. However, thallium is a highly toxic element[10], so it is not suitable for large scale application in industry. In the melting process of bismuth and tin, oxidization burning loss is quite serious on account of the low melting point[11], and thus reduces the yielding rate. The aging strengthening effect of lead-cadmium alloy is weak and short. Therefore, Sb is commonly used to strengthen lead alloys in industry[12]. But Sb and its oxides are toxic and pollute environment[13]. Research shows that alloying lead with aluminum would reduce weight and increase tensile strength[14]. However, these studies mainly focused on the higher Al content[15], and Al mainly exists in the form of precipitates. There is little research about the effect of minor Al on the performance of lead. On the other hand, corrosion resistance of lead alloys has been studied widely, but most of them are concentrated on the battery material[16-19]. The study on corrosion resistance of Pb-Al binary alloy in natural environment is very few.

In the present work, minor Al is added to improve the performance of lead alloys. Pb-Al alloy is melted in vacuum induction furnace and cooled by using forced fast cooling technology. The influence of the concentration gradient of Al on the mechanical properties of Pb-Al alloy was studied by mechanical property test and microstructure observation, meanwhile, the influence of the concentration gradient of Al on the corrosion resistance was studied by artificial atmosphere-neutral salt spray corrosion test.

2. Experimental

The chemical compositions of different Pb-Al alloys are shown in Table 1. In order to prevent the high temperature oxidation of alloying elements and avoid the environmental pollution caused by the volatilization of lead, the melting process is carried out in a vacuum induction furnace. The melting alloy are cast into 10kg ingots under the protection of argon. In the casting process, the mold is cooled by flowing water in order to accelerate the solidification of the liquid alloy, thereby preventing the gravity segregation and grain boundary segregation of Al.

Table 1. The chemical compositions of Pb-Al alloys

Specimens	Al / wt%	Pb / wt%
Pure lead	-	99.999
Pb-0.05Al	0.05	Bal.
Pb-0.10Al	0.10	Bal.
Pb-0.15Al	0.15	Bal.

2.1. Mechanical properties test

The ingots were forged into 17mm cross-sectional bars at room temperature, and then were processed into a variety of test specimens. Standard samples were used for tensile and impact tests. The impact test temperatures were 20°C, -20°C, and -40°C. Breaking the tensile test sample along the axial direction by using the electric spark line cutting, and metallographic specimen was prepared by cold setting in order to avoid that the microstructure of the alloy is affected by high temperature and high pressure. Sample was eroded by a mixed solution (glycerin: glacial acetic acid: hydrogen peroxide; 4: 1: 1), and the microstructure was observed by optical microscopy.

2.2. Salt spray corrosion test

The ingot was rolled into a sheet of 1 mm in thickness by cold rolling mill, and samples with a size of 50 mm×50 mm were cut from the sheet. The sample surface was mechanically-polished and washed in an ultrasonic bath of acetone. The neutral salt spray atmosphere (5%NaCl water solution) was chosen as artificial fog in this experiment. Salt spray corrosion was carried out in salt spray test chamber, with the temperature controlled at 25°C± 1°C. Non-test surface of the sample was wrapped by silica gel so as to improve the accuracy of weight loss measurement per unit area. The treated samples were placed in four corners of the salt spray test chamber. The surface morphology changes were observed regularly. After the test, the samples were soaked in hydrochloride aqueous solution (volume ratio, 1:1; ρ=1.18g/mL), adding CH12N4 as a corrosion inhibitor, to remove corrosion products. The samples were cleaned with water and acetone at room temperature. After rapid drying, measured sample weight and calculated the quality loss per unit area. The morphology of etched surface was observed by optical microscope and the effect of Al element content on corrosion morphology was analyzed.

3. Result and discussion

3.1. Microstructure

At room temperature, lead and lead alloys consist of the alpha phase (Pb) and the terminal solid solution based on other elements. The microstructure of lead alloys with different Al contents is shown in Figure 1. There was no significant difference between the alloys with different Al. The Microstructures of all alloys were twin structure, and the twin structure was gradually refined with the increase of Al content. Research shows that the grains of Pb alloys were refined with 0.01-0.08% aluminum addition[20]. As aluminum content increased to 0.15%, the lead alloy grains were further refined in the present work. Moreover, there were obvious precipitates in grains of Pb-0.15%Al alloy. The solubility of Al in Pb was lower than 0.10% at room temperature[21]. Therefore, the addition of excess aluminum may produce Al-rich phase.

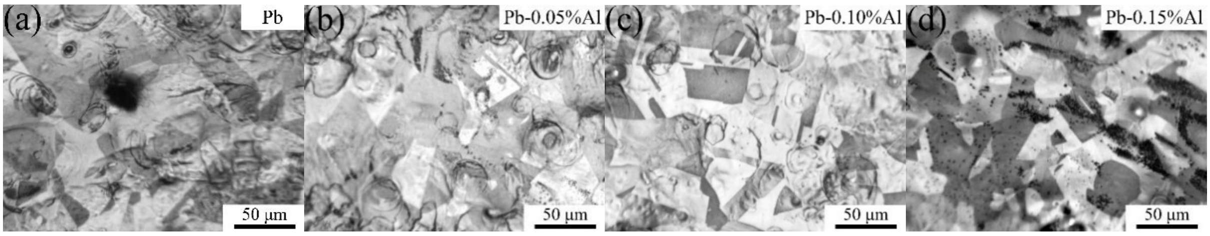

Figure 1. The microstructure of Pb-Al alloys: (a)Pb; (b)Pb-0.05%Al; (c)Pb-0.10%Al; (d)Pb-0.15%Al

3.2. Mechanical property

The mechanical properties of pure lead and Pb-Al alloys are shown in Table 2

Table 2. Mechanical properties of Pb-Al alloys

Specimen	R_m / MPa	A / %	Z / %	A_{KV}/ J		
				20°C	-20°C	-40°C
Pure lead	13.2	75.3	100	18.0	18.3	18.5
Pb-0.05%Al	17.9	73.7	100	19.5	20.2	20.2
Pb-0.10%Al	15.5	78.2	100	17.4	18.7	19.2
Pb-0.15%Al	16.5	80.5	100	18.8	19.0	19.5

3.2.1. Tensile property. The mechanical properties of lead alloys changed obviously with the increase of the content of Al. The tensile strength of Pb-0.05%Al alloy was the highest, which is 17.9 MPa. The strength of lead alloys appeared to fluctuate with aluminium content increasing. But it showed the enhancement effect overall. Compared with pure Pb, the strength of Pb-0.05%Al, Pb-

0.10%Al and Pb-0.15%Al alloys increased by 4.7 MPa, 2.3 MPa and 3.3 MPa, respectively. It can be seen that the strengthening effect of Al element on Pb was obvious.

Section shrinkage rates of pure lead and three lead alloys were all 100%. Although the elongation of Pb-0.05%Al alloy decreased slightly compared with others, but it still exceed 70%. The result showed that the addition of Al element has little influence on the plasticity of the alloy, while increasing the strength of the lead alloy.

3.2.2. Impact toughness. As can be seen in Table 2, impact energy of Pb and Pb-Al alloys were all improved with the decrease of the temperature. Compared with other alloys, Pb-0.05%Al alloy had the highest impact toughness. The impact energy was decreased with Al content was further increased to 0.10% and 0.15%, but the low temperature impact energy was slightly higher than that of Pb. It showed that the low temperature impact toughness of Pb-Al alloy can be improved by adding Al element.

The main factors affecting the impact toughness are grain size, microstructure, and macro-fiber flow and so on. And the grain size is the main influencing factor. The smaller the grain size of the metal material, the higher the impact energy, and vice versa reduced. The recrystallization temperature of Pb and Pb-Al alloys is below zero. Above the critical point of recrystallization temperature, the grain of Pb-Al alloy has a tendency to grow up with the increase of temperature. However, coarse grains can lead to the reduction of impact energy. Therefore, the impact energy that is measured in the experiment will be decreased with the increase of the temperature. Pb-Al alloys were not broken after impact test at different temperatures. This shows that Pb-Al alloys had better stability at low temperatures.

3.3. Salt spray corrosion test

3.3.1. Macroscopic morphological. Figures 2 and 3 are the macro photos of the samples after the salt spray corrosion. As shown in Figure 2, the surface of the sample was lost and the colour gradually faded after 2h corrosion. From the colour of the corrosion film, the surface of pure lead was the most uneven. It showed that the thickness of the product is not uniform, and accompanied with drops phenomenon. Compared with pure lead, the surface color of Pb-0.05%Al and Pb-0.10%Al alloy were more uniform. When further increasing the Al content reached 0.15%, the surface of the sample was relatively rough. But there was no obvious change in the color of the corrosion film at different locations. The thickness and composition of the product are the main reasons for the change of the surface color, so it can be concluded that the corrosion resistance of Pb-0.05%Al and Pb-0.10%Al alloy is slightly different from that of lead. However, due to the limitations of the experimental conditions and objectives, the specific product did not carry out quantitative analysis and further research is needed to determine it.

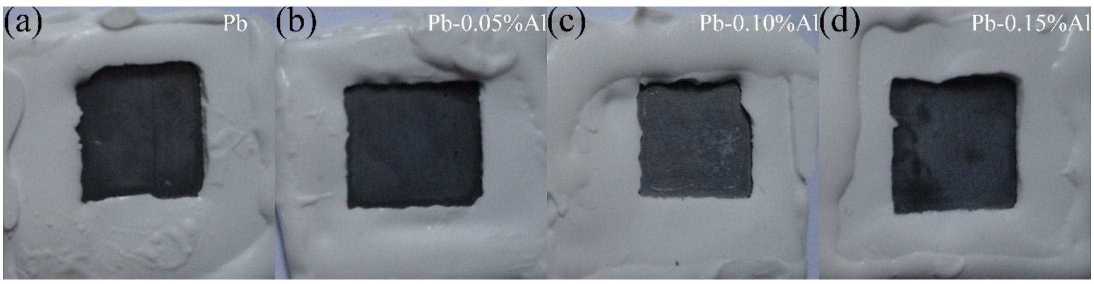

Figure 2. Macrographs of Pb-Al alloys after 2h corrosion: (a)Pb; (b) Pb-0.05%Al; (c) Pb-0.10%Al; (d) Pb-0.15%Al

Macrographs of Pb-Al alloys after 96h corrosion are shown in Figure 3. From figure 3(a) and 3(d), we can see that the colored corrosion film was formed on the surface of Pb and Pb-0.15%Al alloy. And there existed a certain amount of corrosion groove on the substrate of the two alloys. Compared with the sample after 96h corrosion, the surface roughness of Pb-0.15%Al alloy was deeper and the surface became dim after 96h corrosion. Although there was a certain product film off on the surface of Pb-0.5%Al and Pb-0.10%Al alloy, the color change was not obvious. The result showed that the product film was still relatively uniform and the binding force of the membrane and the substrate was strong after long time corrosion.

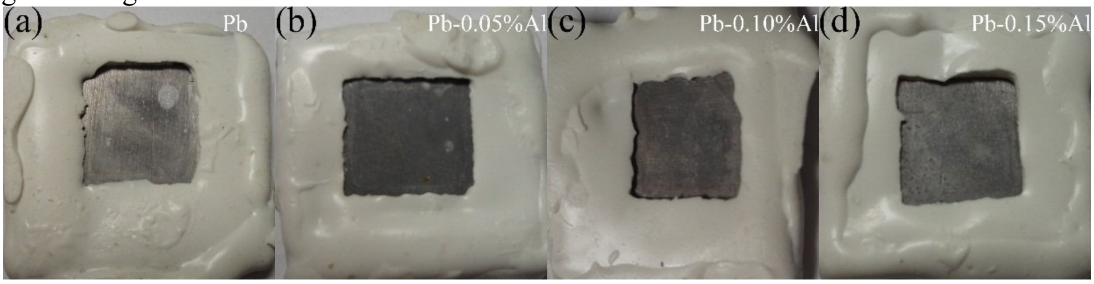

Figure 3. Macrographs of Pb-Al alloys after 96h corrosion: (a)Pb; (b) Pb-0.05%Al; (c) Pb-0.10%Al; (d) Pb-0.15%Al

3.3.2. Mass loss. Mass loss of Pb and Pb-Al alloys after 96h corrosion is shown in Table 3. As can be seen from Table 3, the values of mass loss per unit area of Pb and Pb-0.15%Al alloy unit area were 12.5mg/cm^2 and 10.5g/cm^2, respectively; as for Pb-0.05%Al and Pb-0.10%Al alloys, they were 5.7mg/cm^2 and 4.3mg/cm^2, respectively. Compared with Pb and Pb-0.15%Al alloy, Pb-0.05%Al and Pb-0.10%Al alloys have higher corrosion resistance.

Table 3. Mass loss of Pb-Al alloys after 96h corrosion

Specimen	Pre-test quality/mg·cm^{-2}	Post-test quality/mg·cm^{-2}	Mass loss/ mg·cm^{-2}
Pure lead	3940.8	3928.2	12.5
Pb-0.05%Al	4994.9	4989.2	5.7
Pb-0.10%Al	4504.4	4500.1	4.3
Pb-0.15%Al	4940.2	4929.7	10.5

Compared with Pb, the mass loss of Pb-0.05%Al and Pb-0.10%Al alloy decreased by 6.8mg/cm^2 and 8.2 mg/cm^2 after 96h corrosion, respectively; as for Pb-0.15%Al, by contrast, it only decreased by 2mg/cm^2. The result shows that the corrosion resistance of Pb-0.05%Al and Pb-0.10%Al is more than twice that of Pb.

3.3.3. Microstructure. After 96h corrosion, there were a large number of ditch corrosion and a certain number of corrosion pits on Pb surface, and its size is larger, as shown in Figure 4(a). Compared with Pb, the number of ditch corrosion and corrosion pits of Pb-0.05%Al and Pb-0.10%Al were significantly less, as shown in Figure 4(b), 4(c). However, when the Al content is further increased to 0.15%, their numbers were significantly increased, as shown in Figure 4(d). By comparing the microstructure changes and mass loss, it is found that the variable tendency of the weight loss and the number of ditch corrosion and corrosion pits on the surface of Pb alloy is consistent. When the number and size of ditch corrosion and corrosion pits were increased, the weight loss became larger, and vice versa.

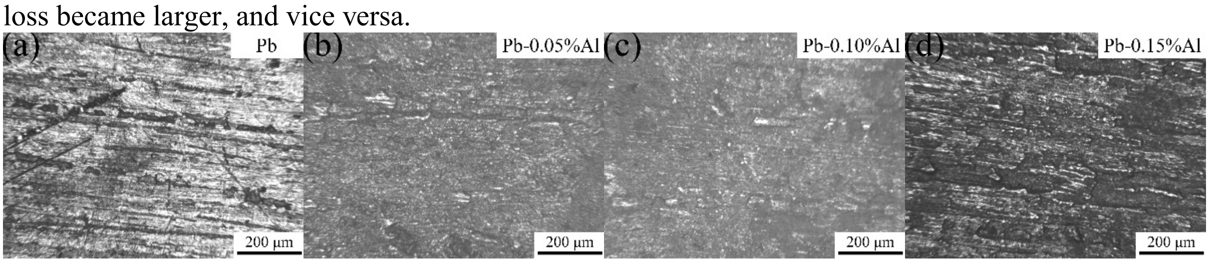

Figure 4. Micrograph of Pb-Al alloys after 96h of corrosion: (a)Pb; (b)Pb-0.05Al; (c)Pb-0.10Al; (d)Pb-0.15Al

3.3.4. Mechanism of salt spray corrosion. Fmoreas been carried out to study the effect of alloying elements on the corrosion resistance of lead[16]. Lead based solid solution is formed by adding a small amount of alloying element, such as tin, antimony, bismuth, aluminium. As stated above, not only can it improve the mechanical properties of the alloy, but also help to improve the corrosion resistance[9]. However, adding excessive alloy elements may harm the corrosion resistance of lead alloys[22].

The addition of excess aluminium may produce Al-rich phase, as shown in figure 1(d). And it enables the formation of a local micro cell between the lead base and the Al-rich phase. Anodic lead dissolution under the action of positive and negative ions in aqueous solution, and a certain amount of oxidation products was generated on the surface. Eventually, ditch corrosion and corrosion pits were formed. Although pure water has no effect on lead, dissolved matter in water may lead to surface erosion of lead. Corrosion in aqueous solution occurs in an electrochemical process. Lead atoms enter the solution with a metal cation state or transition into solid state compounds at the anode. In the neutral salt solution, the cathodic reaction is the reduction of dissolved oxygen.

In the neutral salt solution, Cl^{-1} in water is not directly involved in chemical reactions. But it accelerates the corrosion of the lead matrix in the whole process of the reaction. In the case of a certain concentration of Cl^{-1}, the higher the content of Al in the alloy, the more intermetallic compounds are formed. And then the galvanic reaction of the alloy is stronger. Finally, the weight loss is increased in the process of salt spray corrosion.

4. Conclusions

(1) The microstructures of lead and all lead alloys were twin structure, and the twin structure was gradually refined with the increase in Al content. And there were obvious precipitates in grains of Pb-0.15%Al alloy.

(2) The strengths of lead alloys were significantly improved after adding Al element. Compared with pure lead, the tensile strength of Pb-0.05Al alloy was increased by 31%, reaching 17.9MPa. And the addition of Al had little influence on the plasticity.

(3) The addition of Al could significantly improve the low temperature impact performance of lead, especially in Pb-0.05%Al alloy. The impact energies of Pb and Pb-Al alloys were increased with the decrease in temperature, and there was no low temperature embrittlement phenomenon.

(4) The corrosion resistances of Pb-0.05%Al and Pb-0.10%Al alloys were significantly increased compared with pure lead. However, the mass loss of Pb-0.15%Al alloy was similar to pure lead. It indicated that the solid solution of aluminium in lead lattice can effectively improve the corrosion resistance of lead alloys. But excessive Al could easily form an Al-rich phase which leads to the local micro cell effect and accelerate the corrosion of Pb matrix.

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