Effects of Alloying Elements on Flash Points of Lead

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The measurement was made of the flash points, viz., the temperature at which lead and lead alloys suffer heavy corrosion and disintegration in a concentrated sulphuric acid solution. It was observed that the addition of alloying elements within the limit of solubility lowers the flash-point of lead alloys. Their effect may be classified as follows: With the increasing amount of the alloying element, the flash-point of lead alloys is

- (1) lowered markedly: e.g. Bi, Sb, Sn, Zn
- (2) lowered at first and then increased, but its temperature is lower than the flash-point of pure lead: e.g. Ag.
- (3) lowered at first and then increased, resulting in a higher flash-point than that of pure lead: e.g. Ni, Cu, Te.

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I. Introduction

Lead and lead alloys are widely used as a high resistant metal and alloy to sulphuric acid, but the measurement of corrosion resistance for sulphuric acid by the immersion test is usually time-consuming⁽¹⁾, and in most cases it is difficult to perform a long duration corrosion test. G. Lunge⁽²⁾ discovered that there is a great difference in the temperatures at which leads of varying purities suffer heavy corrosion and disintegration when they are heated in concentrated sulphuric acid solution, and this particular temperature is named the flash point of lead. This test procedure is proposed as a short duration test of corrosion re-

sistance to sulphuric acid of lead.

The authors have measured the flash points of lead and lead alloys containing small quantities of various alloy elements in order to make clear the effect of alloy elements on the flash-point of lead.

II. Experimental Method

For the corrosion test, pure metals such as lead, bismuth, tin, zinc, antimony, tellurium, copper, nickel or silver, and lead alloys with one of these elements, 1 cm³ (1 cm cubic) in size, were placed in a 100 cc conical beaker containing 50 cc of concentrated sulphuric acid solution (Sp. Gr. 1.84) and a thermometer was inserted in the solution. The heating was carried out at the rate of 40°C/min. The temperature at which these metals and alloys were broken up or the resulting corrosion products were exfoliated and the solution was violently flashed was measured as

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(2) G. Lunge; Z anorg allg Chem., 5 (1892) 642.

the flash-point.

III. Experimental Results

1. Flash-points of lead and lead alloys

The flash-points of 99.9999% Pb (zone refined lead), 99.99% Pb (electrolytic lead whose impurities were measured by chemical analysis) and each lead alloy are shown in Table 1 and Figs. 1~8. The flash-points of the alloys of impure lead containing varying amounts of copper are shown in Table 2, and the flash-points of lead bismuth alloys containing copper, tellurium, nickel or silver are shown in Table 3, and the flash-points of lead-antimony-copper and lead-bismuth-copper alloys are shown in Table 4.

The process of disintegration of each alloy is as follows.

99.9999% Pb

At about 160°C, small bubbles began to appear on the surface of the lead, and the surface turned yellow. This was assumed due to the decomposition of sulphuric acid at a high temperature

and the reaction between lead and oxygen in the nascent state formed yellow PbO.

As the temperature reached about 200°C, the yellow-

Table 1 Flash-Points of lead alloys.

Alloy %	Bi	Sn	Zn	Sb	Te	Cu	Ni	Ag
Electrolytic lead	305	305	305	305	305	305	305	305
0.0015	303			280			304	
0.003	303	295	280	275	264		304	
0.005	303		280	260	258	304		301
0.006	303	295	280	253		303	303	
0.01	300				274	303	305	300
0.013	296	295	277	253			310	
0.025	295	297	280	235		303	314	265
0.04	285	296			300	302	316	
0.05	285	293	278	235				265
0.06					309	315	316	
0.07	276							270
0.08					315	315	316	
0.10	160	293	272	225	>315	315	316	275
0.20	160	293	263	225				276
0.30		260						279
0.40		260						284
0.50								284
0.80		235						
1.00								285
10.0					>317			
pure metal	258	224	311	305	190	>320	>320	280

Table 2 Flash-Point of Pb-Cu alloys.

Chemical composition						Flash point (°C)
Pb %	Sb+Sn %	Ag %	Bi %	Zn %	Cu %	
99.96	0.008	0.001	0.03	tr	tr	250
99.92	0.008	0.001	0.03	tr	0.04	302
99.9	0.008	0.001	0.03	tr	0.06	304
99.8	0.008	0.001	0.03	tr	0.08	306
99.8	0.008	0.001	0.03	tr	0.1	308

Table 3 Flash-Points of Pb-Bi alloys, Cu, Ni, Te or Ag.

Quantity of addition	0.08% Cu	0.082% Ni	0.08% Te	0.05% Ag
Alloy				
Pb-0.05% Bi	312			
Pb-0.1% Bi	307	309.5	305	260
Pb-0.2% Bi	294			

Table 4 Flash-Points of Pb-Bi-Cu and Pb-Sb-Cu alloys.

Chemical composition	Flash point (°C)
Pb-0.04% Cu-0.1% Bi	295
Pb-0.1% Cu-0.1% Sb	307

colored oxide film began to disappear, and the surface turned white perfectly at 240°C. The reaction is considered as follows:

As the temperature was further raised up to about 260°C, the white-color lead sulphate film began to break up; and at 311°C it was seen to flash.

99.99% Pb

The process was essentially the same as the above case of the high purity of 99.9999% Pb, but the flash point was at 305°C, slightly lower than in the above case.

Pb-Bi alloys

It was seen that the surface of lead alloys containing 0.1~0.2% bismuth turned yellow at 100~110°C, and they were affected considerably at 140°C. The alloys containing less than 0.04% Bi were so much affected that they were exfoliated at 270~290°C.

Pb-Sb alloys

The surface of 0.025~0.2% Sb alloys turned greyish-black at 70°C, besides which there were no particular changes up to about 220°C.

Pb-Sn alloys

At about 270°C, the white-colored surface was so much affected that it was exfoliated. The lead-tin alloy containing less than 0.2% tin was not easily dissolved until it reached the flash-point.

Pb-Zn alloys

The surface of 0.05~0.2% Zn alloys turned black at about 50°C and yellow at 260°C with a violent

Fig. 1 Effect of bismuth content on the flash point of lead-bismuth alloy.

Fig. 2 Effect of tin content of the flash point of lead-tin alloy.

Fig. 3 Effect of tin content on the flash point of lead-zinc alloy.

reaction. 5% Zn alloy began to produce bubbles at 160°C and to dissolve a little at 285°C. It flashed at 299°C.

Pb-Ag alloys

At 30°C, the surface of these alloys turned black. The occurrence of bubbles decreased as compared with the other alloys.

Pb-Cu alloys

The surface of these alloys turned black at about 50°C and turned white with sporadic bubbles at 250~260°C. The specimens did not suffer disintegration

Fig. 4 Effect of antimony content on the flash point of lead-antimony alloy.

Fig. 5 Effect of copper content on the flash point of lead-copper alloy.

Fig. 6 Effect of tellurium content on the flash point of lead-tellurium alloy.

Fig. 7 Effect of nickel content on the flash point of lead-nickel alloy.

Fig. 8. Effect of silver content on the flash point of lead-silver alloy.

between 302 and 315°C.

Pb-Te alloys

0.03~0.013% Te alloys began to generate small bubbles at about 160°C, and the bubbles appeared very briskly at about 220°C. At the flash-point temperature, the specimen's surface was corroded, and the solution turned white.

In the case of 0.04% Te alloy, bubbles started sporadically from about 260°C, and a rapid reaction took place at 300°C. For 0.08% Te alloy, the sulphuric acid only became slightly whitish and the specimens remained practically unaffected. 0.1% Te alloy had almost no change on the surface at 315°C and sulphuric acid remained colorless.

Pb-Ni alloys

The solution which contain lead alloys containing less than 0.04% nickel showed light-brown color from 150°C, and small bubbles started to appear at about 160°C. The lead alloys with more than 0.06% nickel showed practically no change at the outset, and bubbles began to appear from the lower part at about 230°C. At about 255°C small bubbles appeared over the lower part, and at 310°C bubbles were produced profusely, but the solution remained transparent up to 315°C. The specimens retained their shape until the flash-point.

Pb-Cu-Bi alloys

The surface of Pb-Cu-Bi alloys turned black at 200°C, and the black surface film was exfoliated a little at 268~275°C.

Pb-Te-Bi alloys

Pb-0.082% Te-0.1% Bi alloy started bubbling at about 190°C and produced bubbles profusely at 260°C.

Pb-Ag-Bi alloys

For this alloy, bubbles began to come out at about 200°C, and the specimen was completely disintegrated at 260°C.

Pb-Ni-Bi alloys

This alloy produced bubbles at about 190°C. As the temperature rose up to 300°C, the bubbles came out profusely.

Pb-Sb-Cu alloys

The surface of Pb-0.1% Sb-0.1% Cu alloy turned black at 80°C, and the solution turned light-brown at 160°C. From about 270°C, bubbles came out profusely, and the surface began to be decomposed at 286°C. At 307°C, it was corroded violently.

2. Flash-points of individual alloy element

The flash-points of the pure metals, which were alloyed with lead at the experiment described in 3~1 were measured. The results obtained are shown in Table 1.

Bismuth

At 120°C, the specimen's surface turned black. The specimen began to dissolve at 252°C and broke up at 258°C.

Tin

At 120°C, the specimen's surface turned white. At 140°C bubbles began to come out, and the specimen was broken up at 224°C.

Zinc

Small bubbles began to generate on the specimen's surface at about 90°C, and the solution turned light-brown. From 190°C, bubbles generated profusely, while the color of the solution grew to deeper brown. At 300°C, this condition continued. At 311°C, the flash took place.

Antimony

At about 130°C, small bubbles began to generate. At 180°C, the surface of the specimen turned black, and bubbles were seen to generate violently at 220°C. At 260°C bubbles become more and more profuse. At 305°C, the specimens was disintegrated into antimony sulphate.

Tellurium

At room temperature, the surface of tellurium assumed pink color, and at 110°C the whole sulphuric acid turned crimson. At about 135°C, small bubbles generate so profusely that the specimens became invisible.

From 180°C, large bubbles began to generate briskly and the break-up took place at 190°C.

Copper

When copper was heated in sulphuric acid, the following reaction took place:

(CuO is black and it's melting point is 1,260°C). Hence

and copper sulphate was thus produced. As the temperature was raised rapidly, the black-colored CuO appeared distinctly at 130°C, and white-colored CuSO₄ appeared clearly at 170°C. At 250°C, the solution presented light-green color and boiled at 320°C. However, the copper specimen was not broken up.

Nickel

No change was noted to be occurred by heating, except the formation of a few bubbles at elevated temperatures.

The sulphuric acid containing nickel boiled nearly up to 320°C, but it retained its original shape.

Silver

Between 160 and 250°C, the only change was the appearance of bubbles. More bubbles generate between 270 and 280°C was seen to be the flash-point. As the temperature was further raised, silver was completely dissolved at 310°C.

However, the specimens did not break up so abruptly as lead and its dissolution occurred gradually.

IV. Consideration

When an extremely small amount of a metallic element (less than 0.03%) is added to lead, the flash-point of lead is lowered irrespective of the kind of the metallic element.

As shown in Figs. 1~8, however, the effect of addition of the alloying element in the flash-point of lead may be classified as follows:

1. The flash-point lowers markedly.
 2. The flash-point lowers at first and then rises, but it is lower than the flash-point of pure lead.
 3. The flash-point lowers at first and then rises to be higher than that of pure lead.
- These various processes are determined by the kinds of alloying elements.

(1) The flash-point of lead alloys containing low flash-point metal

When the low flash-point metal was alloyed to lead, the flash-point lowered markedly. This applies to the lead alloys with bismuth, antimony or tin. If a low flash-point metal is alloyed beyond the limit of the solid solubility and produces β phases of high flash-point, the flash-point of alloy rises. This applies to the lead alloys with tellurium.

(2) The flash-points of lead alloys containing medium flash-point metal

The alloying metals which are added within the range of solid solubility lower the flash-point, but an addition in excess of the solid solubility raises the flashpoint.

As the amount of addition increases, the flash-point rises, but it does not rise so much higher than that of alloying metal. This applies to the lead alloys with silver.

(3) The flash-points of lead alloys containing high flash-point metal

When a high flash-point metal is alloyed to lead and is segregated at the grain boundary, the flash-point of this lead alloy rises higher than that of pure lead. This applies to the lead alloys with nickel. If a high flash-point metal exists as segregated particles in the crystal, the crystal grains of lead become extremely fine and the grain boundary per unit area is greatly lengthened, resulting in dispersion of the impurities at the grain boundary, and consequently the flash-point of this lead alloy becomes high. This applies to the lead alloys with copper. There is a case in which the lead alloys with a high flash-point metal reveal the low flash-point. This applies to the lead alloys with zinc.

The effects of a single alloying element on the flash-

points of lead, as described above, may be summarized as follows. When a metal is added to lead within the limit of solid solubility, the flash-point of lead will lower, irrespective of the kind of the added metal.

When a metal is added beyond the limit of the solid solubility and begins to precipitate as β phases, the flash-point of lead will be affected by the nature of β phases or eutectic, provided that the metal is of low solubility.

In the case of a high solid solubility, even though the flash-point of the precipitated β phases is high, the flash-point of this alloy is equal to that of the solid solution.

(4) Effect of third element on the lead alloys of low flash-point

The metal which tends to rise the flash-point of lead affects the lead alloy of low flash-point.

(i) Effect of copper additions on lead-bismuth alloy

According to the equilibrium diagrams of the lead-bismuth, bismuth copper and lead-copper systems, bismuth has a high solid solubility to lead, but the solid solubility of the copper-bismuth and copper-lead systems is negligibly small. As for the ternary system of copper, lead and bismuth, when a small amount of bismuth is alloyed to lead, bismuth is dissolved in lead and the solid solution shows α phase.

The solution may be considered the binary system of α phases and copper

Namely, as shown in Photo. 1, the copper added is located in the center of the crystal grains of lead,

Photo. 1 Pb-0.06 % Cu alloy as cast. $\times 200$

and makes them extremely fine, and thus the grain boundary is lengthened. In consequence, the concentration of bismuth in the solid solution on which is relatively high is reduced, and it is assumed that bismuth does not so much influence the flash-point of this alloy. The flash-point of this alloy is considered to be equal to that of lead-copper alloy.

Accordingly, the copper added is concentrated in the center of the grains of lead, and when this alloy is heated in sulphuric acid, the copper becomes black

copper oxide and then turns to white copper sulphate. Copper sulphate with lead sulphate which is grown out of the matrix forms a film which wraps the specimen and gives a high flash-point.

(ii) Effect of copper on lead-antimony alloy

An extremely small amount of antimony lowers the flash-point of lead greatly. When copper is added to this lead-antimony alloy, a flash-point above 300°C is obtained as shown in Table 4. This result may be explained as follows. Since antimony-copper alloy has a higher melting point than lead, it crystallizes preferentially from molten alloy and acts as nucleus for crystallization of molten lead. It causes the grain refinement of lead-antimony-copper alloy. So the grain boundary increases, and excess antimony in the lead which does not consist nuclei gathers at the grain boundary. As a result, antimony is extremely dispersed.

(iii) Effect of tellurium on lead-bismuth alloy

The equilibrium diagram of the bismuth-tellurium system bears a close resemblance to that of the lead-tellurium system. It makes an intermediate phase having a high melting-point and this intermediate phase has also an exceedingly high flash-point. In contrast to the fact that the flash-points of tellurium and bismuth are 190°C and 258°C respectively, the flash-point of a 50% Te-50% Bi alloy is higher than 315°C, and is close to the boiling point of sulphuric acid, but the alloy does not break up at 315°C.

As shown in Photo. 2, β phase of lead and tellurium precipitates at the grain boundary of fine lead crystals. It is assumed that the ternary alloy of Pb-Te-Bi precipitates an intermediate phase Te-Bi-Pb at the grain boundary and then raises the flash-point.

(iv) Effect of nickel on a lead-bismuth alloy

According to the equilibrium diagrams of bismuth-nickel, this alloy has a higher melting point than bismuth. The flash-point of 40%-Ni-60% Bi alloy is as high as 320°C.

As shown in Photo. 3, β phase of lead and nickel is found at the grain boundary of lead crystals.

Photo. 2 Pb-0.06% Te alloy as cast. $\times 200$

Photo. 3 Pb-0.07% Ni alloy as cast. $\times 200$

It seems that the ternary phase of Pb-Ni-Bi of high flash-point, produced at the grain boundary is prevented from reducing the flash-point by the addition of bismuth.