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PHYSICAL AND CORROSION-RESISTANT PROPERTIES OF RAPIDLY QUENCHED LEAD-ANTIMONY AND LEAD-ANTIMONY-TIN ALLOYS

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ABSTRACT

Molten lead-antimony and lead-antimony-tin alloys were splat quenched in the spinning wheel set up under overhead pressure of 703 g/sq. cm. for preparation of ribbons. Physical properties of ribbons such as density, microhardness, thickness, electrical resistance and melting point were determined. The corrosion resistance properties of the ribbon and bulk alloy were determined by weight loss after immersion in corrosive electrolyte. The potential-time and galvanostatic measurements of these ribbons in 3% NaCl solutions were carried out.

Key words: Lead-antimony alloy, lead-antimony-tin alloy, rapid quenching method

INTRODUCTION

Lead-antimony alloys are widely used in batteries. The metastable alloys are finding application in many industries like electronics and electrochemicals, etc.

Rapidly quenched metallic ribbons are normally associated with metastable phases. Lead-antimony alloy ribbon is reported [1] to show metastable phases at room temperature. Some of the metastable phases in Pb-Sb and Pb-Sn systems have also been reported [2-6] to be retained at room temperature. It is to be noted that the metastable phases do not have low free energies, but owe their existence to a process of kinetic inhibition. Such phases, stable at room temperature, have also been observed in Pb-Bi system [7,8].

Earlier studies [9-10] on Pb-Sb and Pb-Sb-Sn ribbons have shown that rapid quenching increases the corrosion-resistance properties considerably. It has also been shown that thermal ageing at a low temperature increases the corrosion-resistance properties due to certain precipitation effects [10].

The role of alloying addition on the physical and chemical properties of the ribbons is further investigated here.

EXPERIMENTAL

a) Materials

Pure metals like Pb, Sb, Sn, Cu, Ni, Cd, Fe, Si, Al, Cr used in the study were of 99.9% purity. Bismuth nitrate, sodium hypophosphite, sodium borohydride, which were used as impurity sources during melting were of L.R. quality. Small specimens of ribbons coated on top and bottom cross sectional area with bees wax resin so as to expose one sq. cm. area were used for both the potential-time study and galvanostatic anodic polarization in 3% NaCl solution.

b) Corrosion tests

Coupons were immersed for 45 mins. in 50 ml of HCl : HNO_3 mixture, where the concentrations of both HCl and HNO_3 are kept at 5% (v/v), and the corrosion rates determined on weight loss basis after cleaning them in distilled water.

c) Melting of massive/bulk alloy

Four sets of alloys (Table I) had been prepared using the ingredients, mentioned under materials. Melting was conducted in an electric furnace with flux. The alloys were subsequently remelted for further homogenization, before rapid quenching on rotating wheels [10].

d) Electrochemical measurements

The one sq. cm. area of rapidly quenched alloy was immersed in 3% NaCl solution in a beaker and the change in potential with time is recorded with the help of VTVM under galvanostatic anodic polarisation conditions.

e) Determination of physical properties

The structure of the alloy was determined by X-ray diffraction. The surface characteristic property was examined by SEM (200 to 10000). The composition of the alloys was determined by atomic absorption spectrophotometry. The thickness of the ribbon was determined by digital micrometer. The density and m.p. of the alloy were also determined. The microhardness measurements were done using Vickers Hardness Tester at a test load of 5 gm.

RESULTS AND DISCUSSION

Table I shows the chemical composition of the lead alloy ribbons and the corrosion rate in HCl : HNO_3 mixture in the bulk and ribbon states. It is seen from the Table that there was a marked decrease in corrosion rate values in the case of Pb-Sb ribbons while those containing alloying additions revealed marginal reduction. The 80 Pb : 20 Sb ribbon showed lower corrosion rate than other alloys.

Table I: Percentage composition of the alloys and their corrosion rate values as cast (bulk or massive alloy) and ribbon state

No.	Percentage composition of the alloy	Corrosion rate values (g/cm^2) x 10^{-4}	
		Bulk/ Massive	Ribbon
1.	80 Pb - 20 Sb	0.229	0.050
2.	85 Pb - 15 Sb	0.225	0.100
3.	80 Pb - 19 Sb - 0.17 Cu - 0.13 Ni - 0.09 Cd - 0.01 Fe - 0.004 Al - 0.02 Si - 0.002 Cr - 0.07 P - 0.07 B - 0.004 Bi	0.180	0.130
4.	80 Pb - 10 Sb - 10 Sn	0.250	0.200

Table II : Physical properties

Alloy No. (See Table I)	Density (g/c.c.) Bulk	Density (g/c.c.) Ribbon	Hardness (kg/mm^2) Bulk	Hardness (kg/mm^2) Ribbon	Melting point (°C) Bulk	Melting point (°C) Ribbon	Thickness (μm) Ribbon
1	6.55	3.365	12.25	12.25	250	Slightly affected at 400°C	29.4
2	6.75	3.925	9.25	12.25	240	Became brittle at 400°C	36.25
3	6.025	4.115	14.25	8.25	250	Not affected at 400°C	33.4
4	7.75	4.355	6.4	11.25	200	– do –	43.25

Table II shows the physical properties of the Pb-Sb bulk alloys and ribbons. It was seen that density differs marginally in the ribbon state. Reduction in density was more in the case of ribbons of 80 Pb : 20 Sb and 85 Pb : 15 Sb. Ribbon containing impurity elements decreased in hardness while it was only marginal in the case of 80 Pb : 20 Sb and 85 Pb : 15 Sb ribbons. In the case of Pb : Sb : Sn ribbon, there was considerable increase in hardness, probably due to some intermetallic formation of tin. The reduction in the hardness of the impurity-doped ribbons might be attributed to the layer formation tendency and consequent segregation of impurity and Sb in the layer zones. It was also seen that the introduction of alloying elements like Sn, Cu, Fe, Ni, Cd, Sr, Al, P, B, Bi, Cr etc. in Pb-Sb matrix improved the high temperature resistance of these ribbons. These ribbons were not affected even at a temperature of 400°C. It had also been observed that the appearance of layer structure became more pronounced as the Pb-Sb matrix was being doped with various impurity elements (Table III) (Figs. 1 and 2).

Table III : SEM Microstructure of R. Q. Ribbon

Alloy No. (See Table I)	Microstructure / R. Q. Ribbons
3	Homogeneous matrix is observed. Layer structure is prominent. It reveals segregated impurity doped zones (Fig. 1) 1000 x
4	Homogeneous matrix is observed. Layer structure is prominently displayed. It reveals zones enriched in the third alloying element (Fig. 2) 200 x

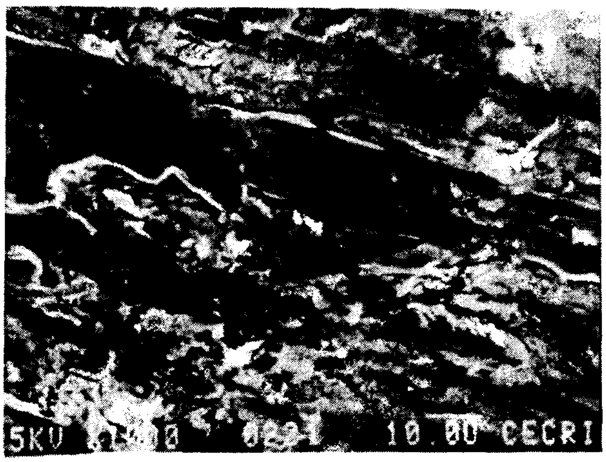

Fig. 1 : Lead + Antimony + Impurity doped, 1000 x

Fig. 2 : Lead-Antimony-tin alloy Ribbon x 200 x

The potential-time graph of these alloys and ribbons immersed in 3% NaCl solution are given in Fig. 3.

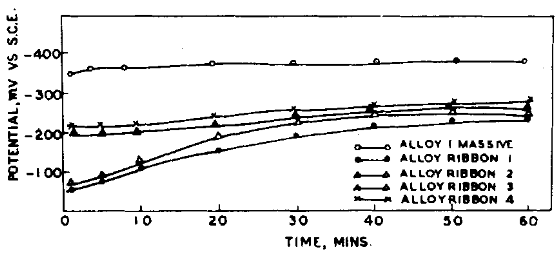

Fig. 3 : Potential vs times in 3% NaCl solution

It was seen that the 80 Pb : 20 Sb ribbon shows more positive value to the bulk alloy. Out of all the ribbons, the 80 Pb : 20 Sb alloy showed more positive potential than other alloys. The addition of impurities in the Pb : Sb matrix did not change the potential values appreciably. The galvanostatic anodic polarisation studies of the ribbons and alloys in 3% NaCl solution are given in Fig. 4 and it may be seen that all the alloys showed very little polarisation.

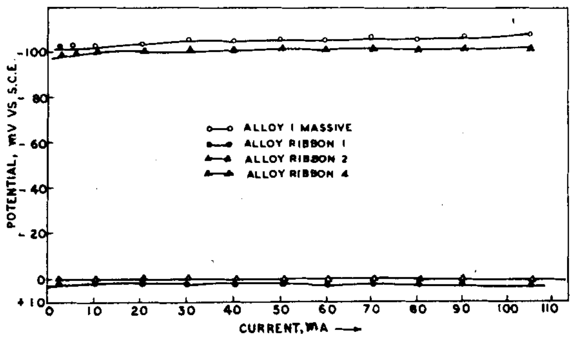

Fig. 4 : Galvanostatic anodic polarization in 3% NaCl solution

The Pb-Sb-Sn ribbon revealed much higher negative potential than the Pb : Sb ribbon having no impurity. The 80 Pb : 20 Sb ribbon showed positive potential and the change of potential with current was little.

Conclusions

The study revealed that impurity doping in the bulk alloy of 80 Pb : 20 Sb did not result in appreciable improvement in the corrosion resistance of these ribbons except the increase in layer formation tendency after splat cooling. The 80 Pb - 20 Sb ribbon appeared to be the most corrosion-resistant of the four ribbons prepared and studied. Rapid quenching increased corrosion resistance of bulk 80 Pb : 20 Sb alloy. The thermal stability of the ribbons were increased as a result of impurity doping.

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