STUDIES ON THE COLD FORMING OF LEAD ANTIMONY THIN METALLIC RIBBON

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The lead antimony metallic ribbon is obtained by splat quenching in melt spinning set up. The dimension of the ribbon prepared is 3 mm x 5 mm x 50 μm thick. The ribbons are compacted, using stainless steel die, under a fixed load for a period of 24 hours. Alternate heating and compacting of the ribbon is also carried out. The ribbons used are lead-antimony (80:20), Pb-Sb (85+15) & Pb-Sb-impurities (80:19.4 : 0.6). One set of composite electrode, is prepared by using Pb-Sb (80:20) ribbon and potential time study is carried out with 1.5% NaCl and 20% H_2SO_4 containing 1000 ppm of chloride ions. The stability of the film is improved by cold-forming and heat treatment. The cyclic voltametric current potential relationship of these thin films have also been obtained after cold-forming and heat-treatment. S.E.M. technique have been employed to study the effect of cold forming and subsequent heat treatment of the ribbon.

Thin metallic ribbons of Pb-Sb, and Pb-Sn systems have been extensively studied by Claude Borromme Guitter [1]. He has reported that during the rapid quenching process some of the metastable phase produced in his study are also retained at room temperature.

Studies conducted in this laboratory on Pb-Sb-Sn metallic ribbons have shown that rapid quenching increases the corrosion resistance properties [2-3] considerably. It has been shown that thermal aging [3] at a low temperature (50° C) increases the corrosion-resistance properties. It has also been observed that impurities [4] doping in the bulk alloy of Pb:Sb (80:20) do not result in appreciable improvement in corrosion resistance of these ribbons, except the increase in layer formation tendency, after splat cooling. However the thermal stability of the ribbons are increased as a result of impurity doping.

In this paper, the authors have studied the role of cold forming and heat treatment separately and in combination. One set of composite electrode is prepared by compacting 10 numbers of the individual ribbons (10 nos). Electrochemical studies of these cold-worked ribbons, have been carried out in 1.5% NaCl and 20% H_2SO_4 containing 1000 ppm Cl^- ion using vacuum tube voltmeter (VTVM) and cyclic voltametric technique. SEM have been used for studying the micro structure, before and after deformation.

EXPERIMENTAL

Materials

Pure metals like Pb, Sb, Cu, Ni, Cd, Fe, Si, Al, Cr, used in the study are of 99.9% purity. Sodium boro hydride, sodium chloride, Trichloroethylene, hydrochloric acid, sodium hydroxide and sulfuric acid of L.R. quality are used.

Small specimens of rapidly quenched ribbons, coated on top and bottom exposing 1 sq.cm. area, are used for the potential time study in 1.5% NaCl and 20% H_2SO_4 containing 1000 ppm Cl^- ion.

Melting of Massive Alloy

Three sets of alloys have been prepared, using the ingredients, mentioned under materials. Melting is conducted in an electric furnace with flux. Molten alloys are cast in graphite blocks. These alloys are subsequently remelted for further homogenization, before rapid quenching on rotating wheels.

Rapid Quenching Process

It compares of simultaneous melting and splating of Pb-Sb alloys on a copper-wheel (rotating at a speed of 3000 rpm), from a stainless steel jet, at a specific temperature for a particular alloy e.g. 250° C for alloy I, 240° C for Alloy II and 250° C for Alloy III (vide Table 1). Pneumatic pressure is applied over

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TABLE 1

PROPERTIES OF Pb-Sb ALLOY IN DIFFERENT CONDITIONS

		Alloy 1 80% Pb 20% Sb	Alloy 2 85% Pb 15% Sb	Alloy 3* 80% Pb 19.4% Sb
Corrosion rate ($g/mm^2/hr)x10^{-4}$	a)	3.913	3.913	5.863
	b)	1.565	1.565	1.690
S.E.M. structure	a)	Layer	Layer	Layer with aggregated impurity doped zone
	b)	Breakdown of layer structure and subsequent redistribution of micro constituents		
Hardness kg/mm^2	a)	12	12	8
	b)	12.5	12.5	13

a) sample as ribbon

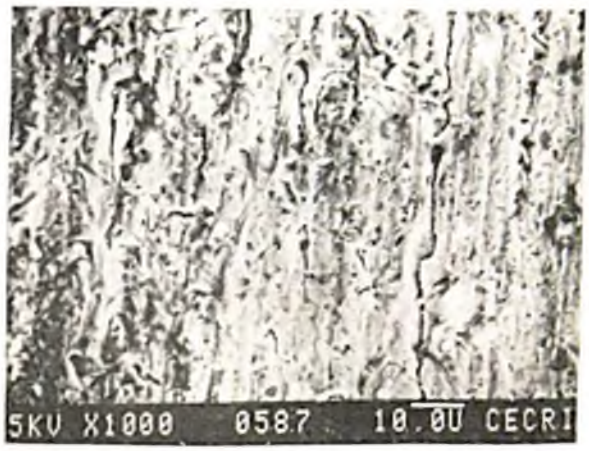
b) Cold pressed and heat treated sample

* Alloy 3 has following impurities Cu 0.17, Ni 0.13, Cd 0.09, Fe 0.01, Al 0.004, Si 0.002, Cr 0.002, P 0.07 B 0.07, Bi 0.004

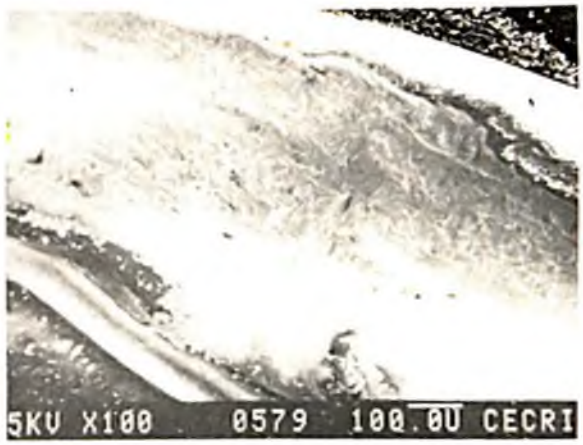
the molten alloy, from a pressure unit, comprising of a compressor and a pressure tank (58 cms diameter), fitted with control valves and pressure indicator. Thirty grammes of the alloy, cut into 2mm x 2 mm piece are melted for a predetermined time and splate quenched on the copper wheel under a pressure of 694.6 Kg/cm^2. Splatting time scarcely exceeded one minute.

Pressing of the Ribbons

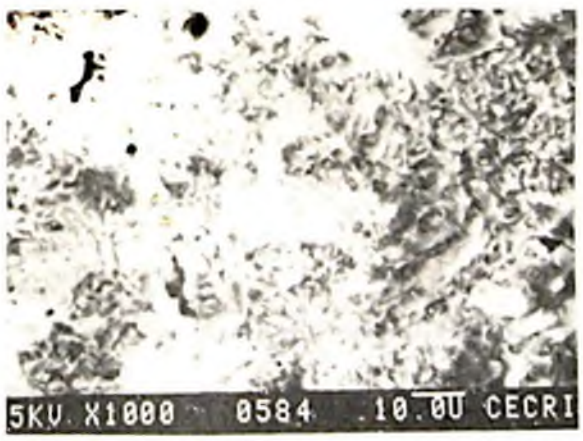
Thin ribbons are pressed (cold deformed) both individually and in a composite form, with the ribbons (one over the other), with the help of a stainless steel die, under a load of 3.97 kg. for a period of 24 hours. For composite electrode, ten ribbons of Pb:Sb :: 80:20 of dimension 3 mm x 0.5 mm x 50 μm are joined together by quickfix at one end and finally pressed the other end. Pressed specimens are heat treated at 50°C for 1 hour, followed by pressing again at 3.97 kg. load for 24 hours. This forms the alternately pressed and heat treated specimen.



(a) No pressing, No heat treatment



(b) Pressed



(c) Pressed and heat treated

Fig. 1 ESE photographs

Aging of the Ribbons

Individual ribbons and the composite electrode are aged at a temperature of 50° C, inside a thermostatically controlled oven, under controlled atmosphere for a period of 45 minutes.

Electrochemical Measurements

The one sq. cm. area of the rapidly quenched individual and composite electrode with and with-out pressing and heat treatment are prepared by masking in Bee`s wax resin. The potential vs time experiemtns are carried out with reference to SCE using a VTVM. Cyclic voltametric study of these electrodes are conducted in 20% H_2SO_4 with 1000 ppm Cl^- ion, with reference to $Hg/HgSO_4$, at a scan rate of 50 mV/sec; scale is set at = 250 mV/Cm and y scale =100 mV/Cm. Potential and current values are obtained from the recorded plots.

The weight loss values (corrosion rate) are determined by using an acid mixture (HCl : HNO_3 : H_2O :: 1:1:8) for a period of 46 minutes.

Physical Properties

The surface characterstics of the alloys are examined in S.E.M. at magnifications at 1000 X. Composition of the alloy is determined by atomic absorption spectroscopy. Hardness values have been determined in Vicker`s Micro hardness testing machine.

RESULTS AND DISCUSSION

Table 1 reveals the composition, microstructure, hardness and corrosion rate values of the rapidly quenched ribbons and their cold pressed heat treated alloys. The bulk alloy reveals Pb-Sb eutectic structure. After rapid quenching and heat treatment, micro-structure reveals some layer formation tendency, and corrosion rate values are reduced. Hardness are not changed in the case of first two alloys but the value increases in the case of impurity doped alloy ribbon.

Figure 1 shows the potential time behaviour of the individual and composite electrodes with and without cold-pressing and heat treatment in 1.5% NaCl solution. It is clearly seen that heat treatment following cold forming, results in more positive potential values, indicating improvement in corrosion resistance properties in 1.5% NaCl solution. Figure 2 indicates similar trends, in 20% H_2SO_4 containing 1000 ppm Cl ion. The potential values are

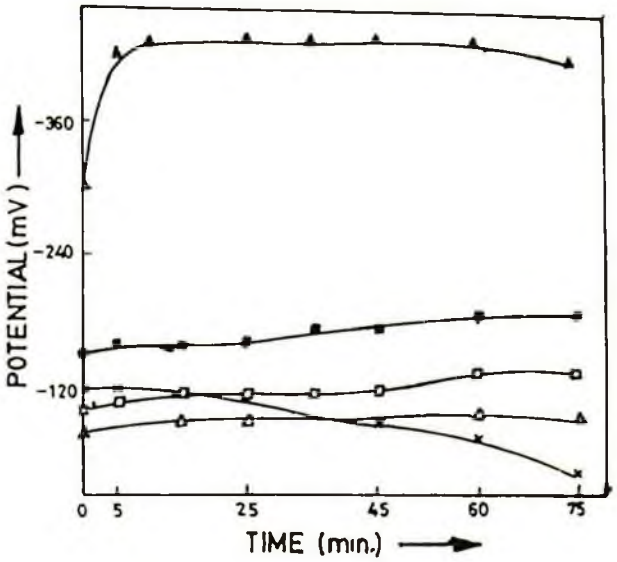


Fig.1 Potential vs time of R.Q. single and composite ribbons in 1.5% NaCl-solution

- △ Pb:Sb 80:20/Composite electrode/pressed
- □ Pb:Sb 80:20/Composite electrode/Alternate pressing and heat treatment.
- ■ Pb:Sb Impurity/single ribbon/No pressing and no heat treatment
- X Pb:Sb Impurity/single Ribbon/pressed
- ▲ Pb:Sb Impurity/Single Ribbon/Alternat pressing and heat treatment

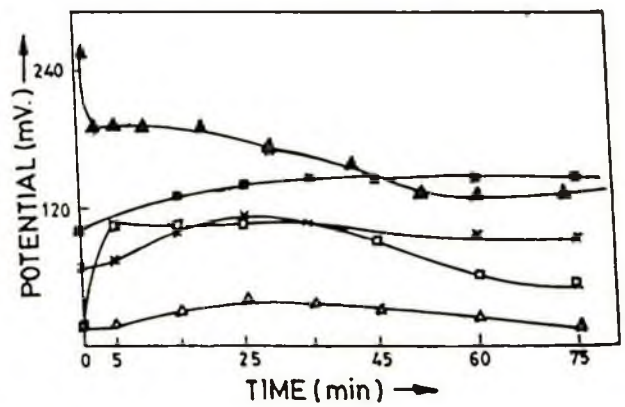


Fig. 2 Potential vs time of R.Q. single and composite ribbons in 20% H_2SO_4 with 1000 ppm Cl

- △ Pb:Sb 80:20/Composite electrode/pressed
- □ Pb:Sb 80:20/Composite electrode/Alternate pressing and heat treatment.
- ■ Pb:Sb Impurity/single ribbon/No pressing and no heat treatment
- X Pb:Sb Impurity/single Ribbon/pressed
- ▲ Pb:Sb Impurity/Single Ribbon/Alternate pressing and heat treatment

more positive than in chloride solution. This is attributed to the composition of the electrolyte, H_2SO_4 solution favours formation of passive film. Heat treatment of the cold pressed specimen results in more positive potentials, indicating that the stability of the film, is also improved, as a result of heat treatment. The performance of single and composite ribbon in 1.5% NaCl and 20% H_2SO_4 with 1000 ppm Cl ion is more or less the same. Positive potentials are obtained for both the cases, and thus reduce the tendency for corrosion.

Table 2 shows the cyclic voltametric current potential relationship. It shows that alternately pressed and heat treated electrodes show lower current than the electrodes without pressing and heat treatment. S.E.M. Micrographs (a,b,c) reveal the Pb:Sb 85:15 ribbons with and without cold pressing and heat treatment. Cold pressing appears to disintegrate the layer structure, while subsequent heat treatment results in further [6] redistribution of the micro constituents.

TABLE 2

CYCLIC VOLTAMTERIC STUDY
IN 20% H_2SO_4 WITH 1000 ppm Cl^- ION

Sl. No.	Potential	Current in Amperes			
		Pb:Sb:85:15 Single R.Q. Ribbon		Pb:Sb: 80:20 Composite electrode (10 Ribbons)	
		a*	b*	a*	b*
1.	- 1.20	0.50	0	0.50	0.30
2.	- 1.25	0.55	0	0.50	0.35
3.	- 1.0	1.65	0	1.6	0.25
4.	- 0.75	0.15	0	0.10	0.20
5.	- 0.50	0.05	0	0.05	0
6.	- 0.25	0.001	0	0.001	0
7.	± 0	0.001	0	0.001	0.15

a) as ribbon.
b) alternately pressed and heat treated.

CONCLUSION

It appears from the study that cold forming and heat treatment improves the corrosion resistance of the rapidly quenched ribbons of Pb and Sb and the composite electrode made of Pb:Sb 80:20 ribbons. Subsequent heat treatment results in redistribution of micro constituents and improvement of the corrosion resistance properties.

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