LBL-32395
UC-404

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

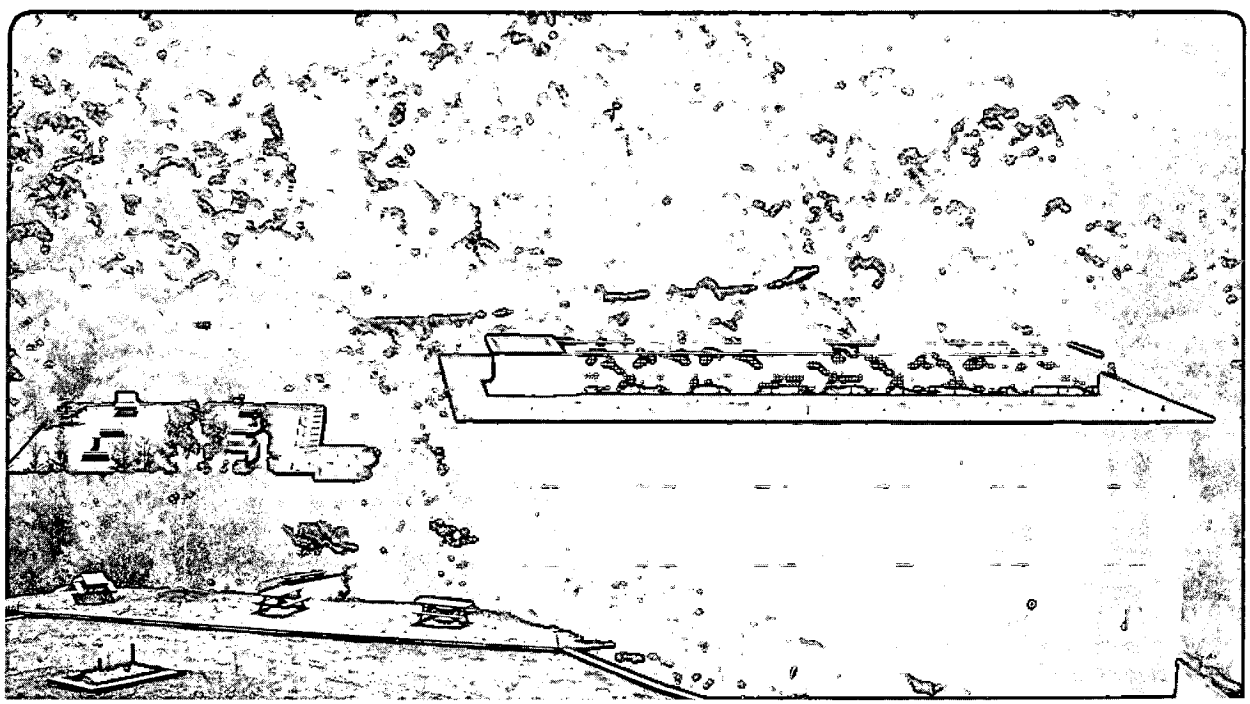
Materials Sciences Division

Presented at the Electrochemical Society Meeting,
Toronto, CANADA, October 11–16, 1992,
and to be published in the Proceedings

Effect of Ion Implantation on the Corrosion Behavior of Lead and Lead-Antimony Alloy

R.H. Muller and S.-T. Zhang

May 1992



REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library.
LBL-32395
Copy 1

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

EFFECT OF ION IMPLANTATION ON THE CORROSION BEHAVIOR OF LEAD AND LEAD-ANTIMONY ALLOY

R. H. Muller and S.-T. Zhang
Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA. 94720

Grid corrosion, particularly in the positive plate, is an important factor that limits the cycle life of lead-acid batteries. It has received considerable attention [1, 2].

In the present work, surface modification by ion implantation has been investigated to reduce the corrosion of grid materials. Titanium was primarily used for implantation; pure lead (99.99%) and a lead-4% antimony alloy were chosen as representative grid materials. The implantation of several other elements produced similar results. Ion implantation has been used before to modify surface properties of metals such as hardness and corrosion resistance [3, 4].

The ion implantation was performed with a new high-current, pulsed ion source that has been described elsewhere [5]. The purity of the Ti arc source was 99.999%. Typical beam current densities were 2.55 mA/cm^2, typical pulse durations 0.24 ms, and pulse frequencies 5-10 Hz. Ion beam energies of 30-120 keV, and implantation doses of $1x10^{15}$ to $5x10^{17}$ $atoms/cm^2$ were used.

Two methods were employed to determine the corrosion behavior of the grid materials: Corrosion rates were derived from the current response of the specimens in 5M H_2SO_4 to small anodic polarization (3-10 mV), extrapolated from short-term measurements to zero time (in order to represent the behavior of the original surface). Also, the morphology of the corroded surface after extended (60 h) open circuit immersion in the sulfuric acid was determined by SEM.

The dependence of corrosion currents for lead and lead-4% antimony on titanium ion dose and energy is illustrated in Figs. 1 and 2. Optimum implantation conditions are slightly different for the two specimens but lie in the vicinity of $5x10^{16}$ $atoms/cm^2$ and 60 keV. Compared to the untreated specimens, corrosion currents are reduced by the ion implantation up to 36-fold for the pure lead and up to 72-fold for the lead-antimony alloy.

The effect of the implantation of some other ions on corrosion currents is comparable to that of titanium and is illustrated in Table 1 for one set of implantation conditions.

Depth profiles of the implanted ions, obtained by Auger spectroscopy, are shown in Fig. 3. These profiles compare well with computed profiles and, together with anodic and cathodic polarization measurements, provide mechanistic information on the effect of ion implantation

REFERENCES:

[1] V. Daniel and V. Plichon, Electrochim. Acta **20**, 781 (1983).

[2] Y.-L. Guo, J. Electrochem. Soc. **138**, 1222 (1991)

[3] I.G. Brown, M.R. Dickinson, J.E. Galvin, X. Godechot and R.A. MacGill, J. Materials Eng., **13**, 217 (1991).

[4] D. Gorse, B. Rondot and Y. Serruys, Corros. Sci..**31**, 685, (1990).

[5] I.G. Brown, M.R. Dickinson, J.E. Galvin, X. Godechot and R.A. MacGill, 7th International Conference on Surface Modification of Metals by Ion Beams, Washington, DC, July 15-19,1991.

ACKNOWLEDGMENTS

We thank I. G. Brown for his help with the use of the ion implantation equipment.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Table 1. Effect of the ion implantation of different atoms on the corrosion of lead and lead-4% antimony alloy in 5 molar sulfuric acid.

Implantation Conditions						Corrosion Current mA /cm^2	
Ion	Energy keV	Dose atoms /cm^2	Peak Current Density mA/cm^2	Pulse Duration ms	Pulse Frequency Hz	Pb	Pb-4%Sb
Ti	60	5x10^{16}	2.55	0.24	5	0.15	0.040
V	60	5x10^{16}	2.55	0.24	10	0.20	0.053
Cr	60	5x10^{16}	2.55	0.24	10	0.27	0.093
Ni	60	5x10^{16}	2.55	0.24	10	0.18	0.085
W	180	5x10^{16}	2.55	0.24	~3	0.81	0.51
none	-	0	-	-	-	5.4	2.9

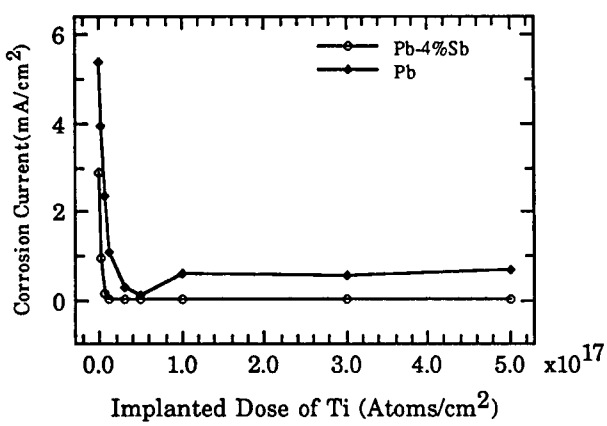


Fig.1 Dependence of corrosion current of Pb and Pb-Sb on dose of Ti implantation conducted at 60 keV.

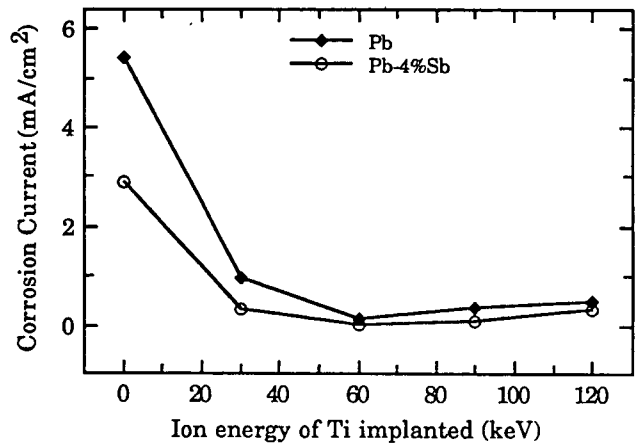


Fig.2 Dependence of corrosion current of Pb and Pb-Sb on Ti ion energy of implantation at 5x10^{16} atoms/cm^2.

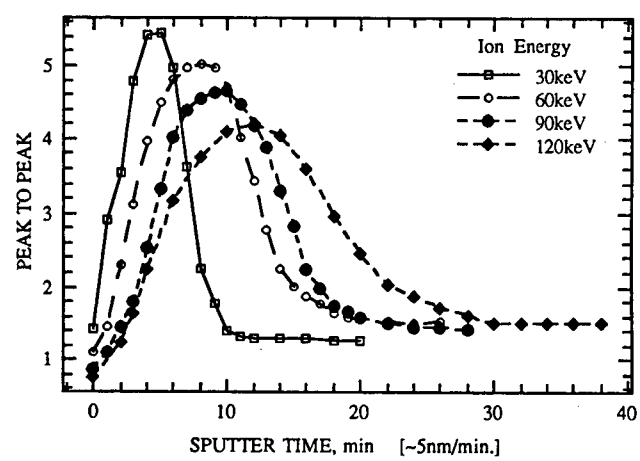


Fig.3 Measured depth profiles of Ti distribution in Pb for different implantation energies and a dose of 5x10^{16} atoms/cm^2.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720