"Past AESF Projects and Some New Directions"

Howard W. Pickering

AESF Students

Kai Wang (PhD) Ahman Zaky (MS) Dan Marx (MS) Lucille Giannuzzi (PhD)
Sury Kaja (PhD) Eric Maurer (MS) Ani Simsek Gokcesu (MS) Joel D. Katz (MS)

Co-Workers

Drs. Konrad G. Weil, William R. Bitler and Paul R. Howell

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

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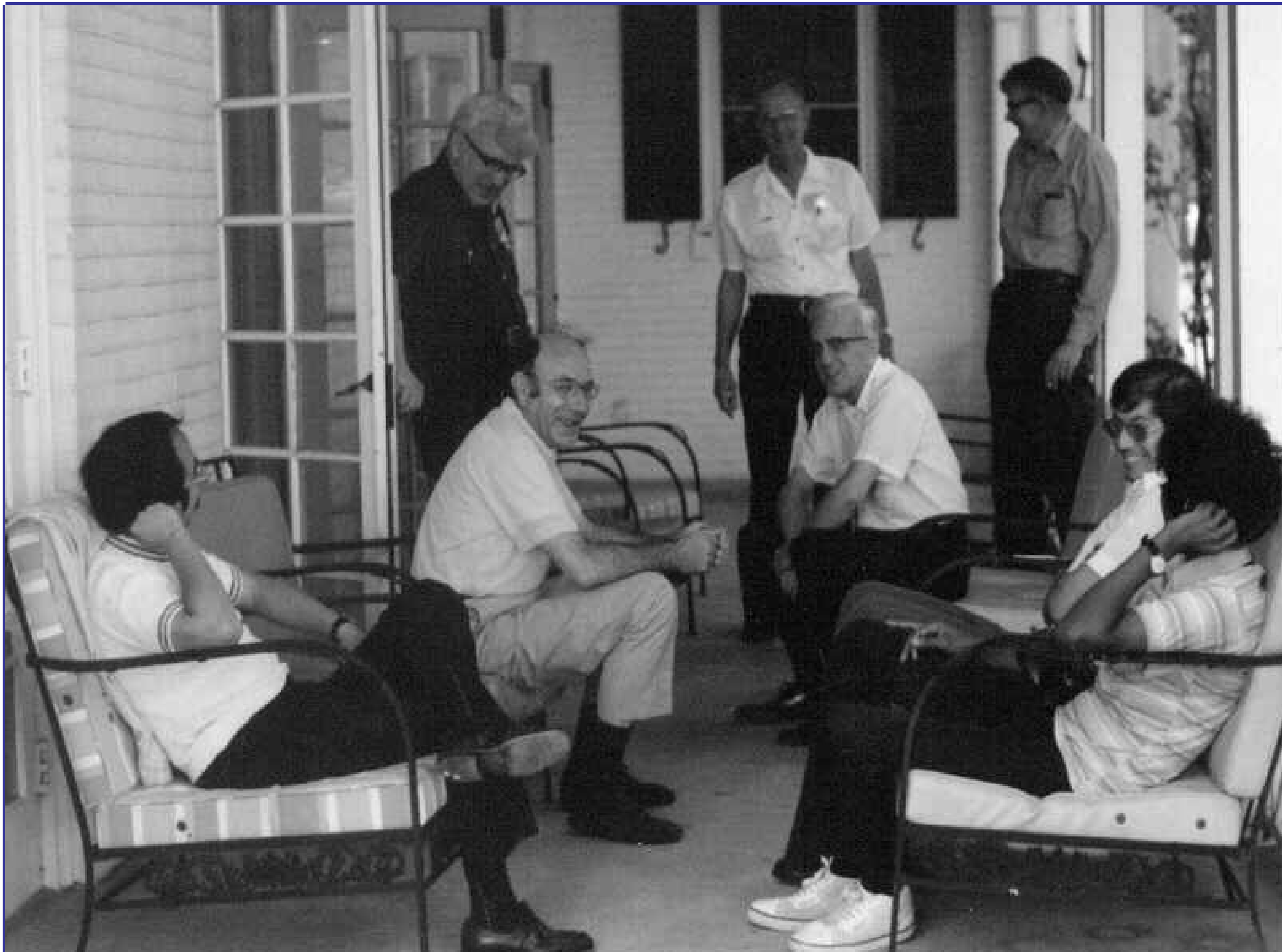
Sponsors: AESF, ONR, NSF

Read Conferences: 1965 - 1994

Dr. Harold Read, second from right, professor emeritus of metallurgy, served as honorary chairman of the 4th Penn State Conference on Electrodeposition which was held at Penn State's University Park Campus last summer. With him here are four alumni of the College of Earth and Mineral Sciences who were among the 63 scientists and engineers who attended the conference (left to right): Richard Wedel of the Shipley Company, Newton, Mass., who received his Ph.D. in fuel science in 1969; Rolf Weil of Stevens Institute of Technology, Hoboken, N.J., who received his Ph.D. in metallurgy in 1951; Arthur H. Graham of DuPont, Wilmington, Del., who has three degrees in metallurgy, having

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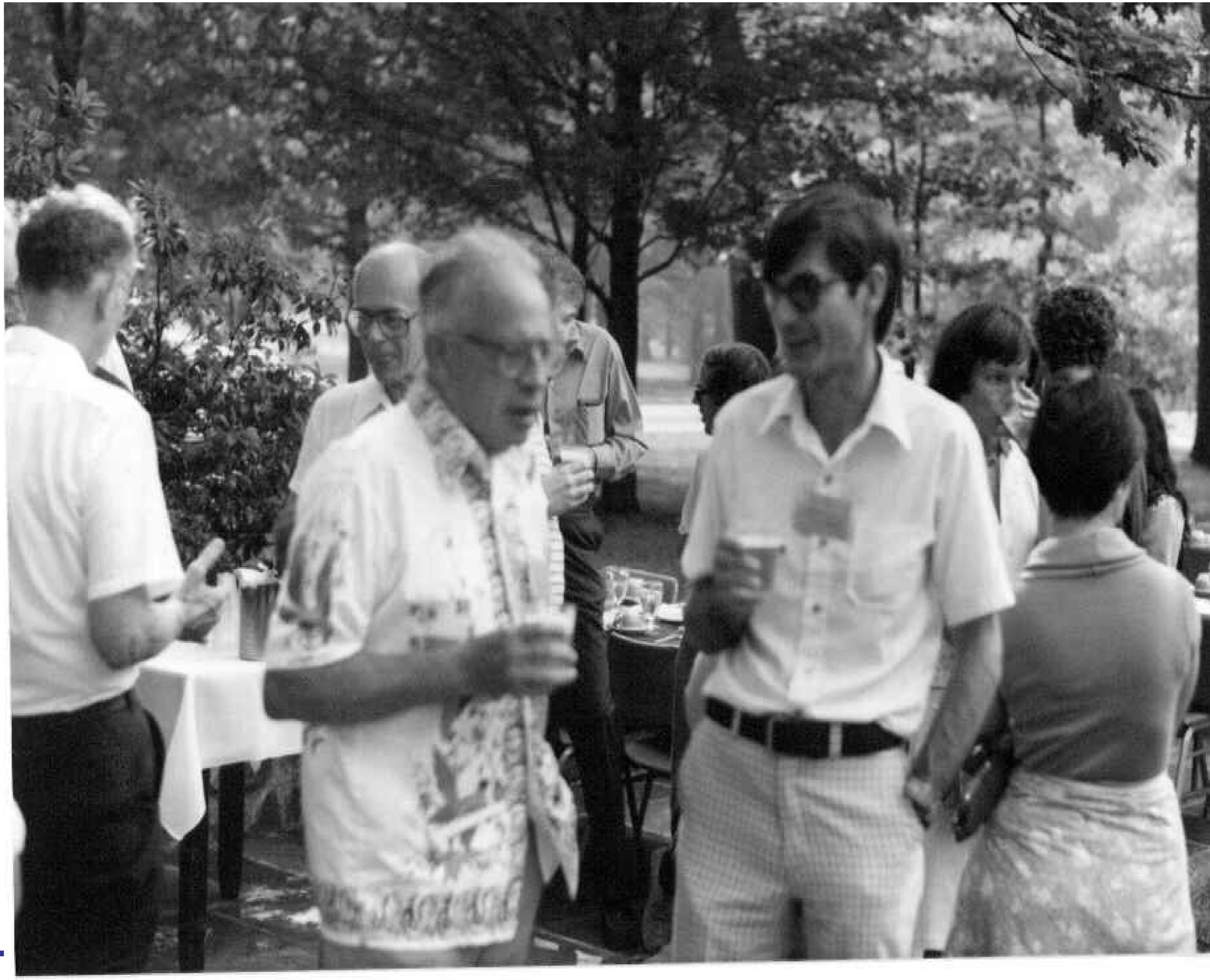

Reasons for Diffusion Studies in Au, Pd and Ni Overplates on Copper

- Miniaturization leads to more corrosion of electronic devices.
- Thinner overlays lead to cost savings.
- Tarnish films increase contact resistance and electronic noise.
- Characterization of metal barriers and overplates to increase lifetimes.

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Findings

- Co and Co-P are effective barriers for Au on Cu at high temperatures (750-950 °F), comparable to Ni-P and better than electroplated Ni.
- Lower bath pH decreased Ni plating efficiency and grain size: Cu penetration increased.
- In a lower °F range, a different diffusion mechanism (grain boundary) operates. It gives less Cu penetration as temperature and time increase. How can this be?

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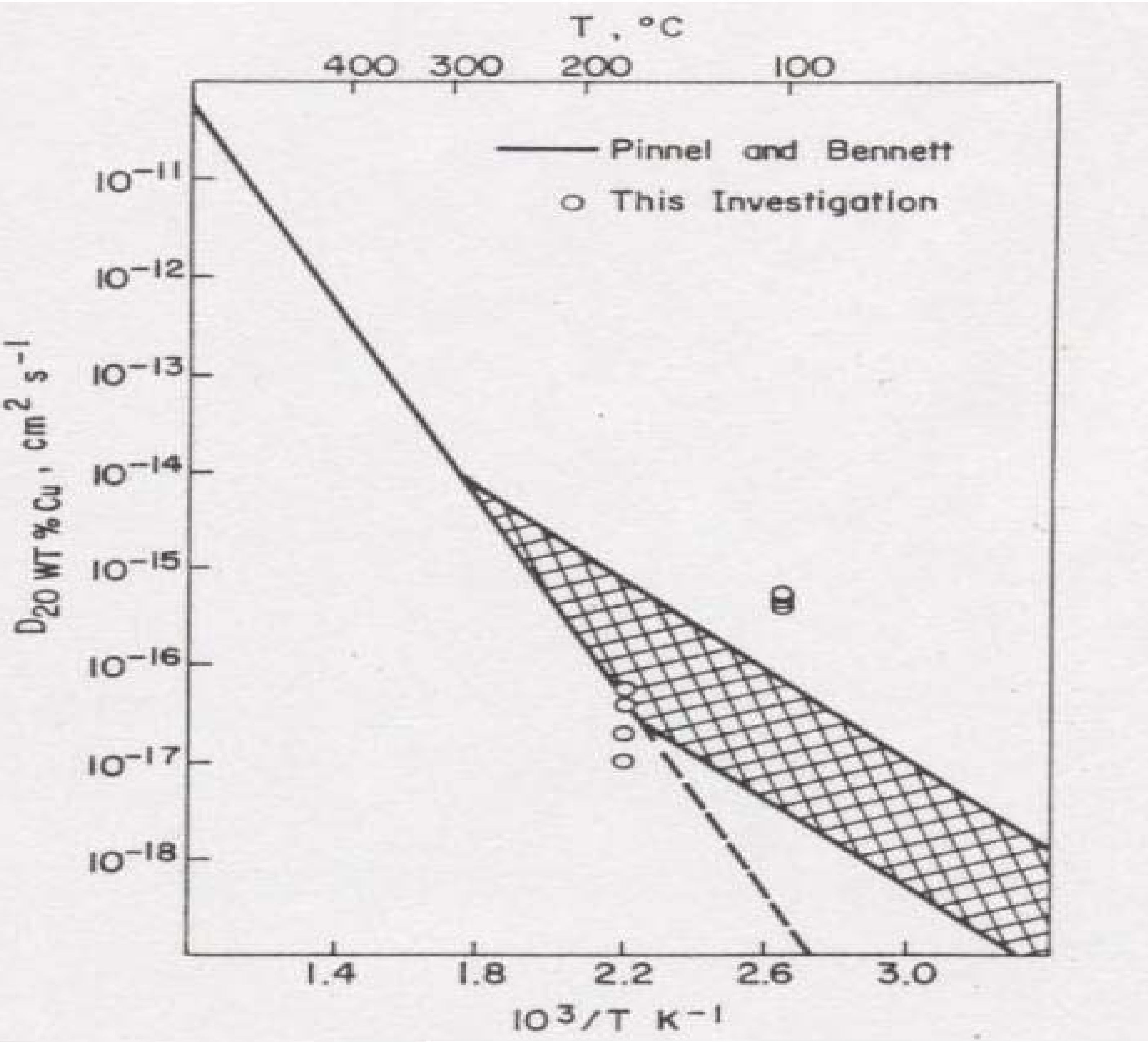

T , °C
400
300
200
100
Pinnel and Bennett
This Investigation
D_{20} WT % Cu , $cm^2\ s^{-1}$
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
10^{-18}
1.4
1.8
2.2
2.6
3.0
$10^3/T\ K^{-1}$

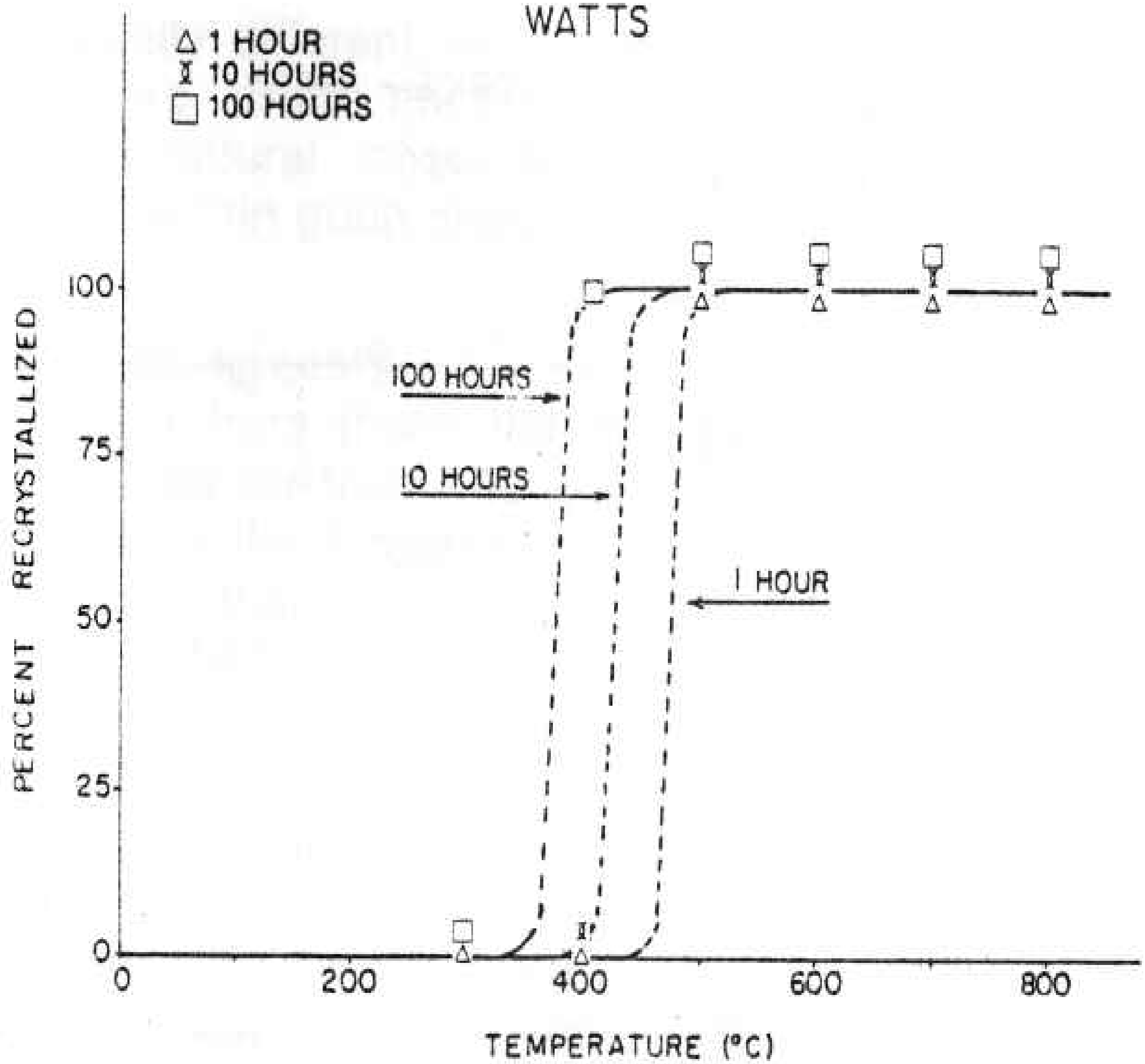

Fig. 3—Recrystallization curves for Watts electrodeposits.

Table IV
Time at 300° C For Complete Recrystallization

Chloride-free, sulfamate	58 hr
Watts	5.089×10^{4} hr (6 yr)
All-chloride	5.509×10^{6} hr (629 yr)
Nickel-60% deformation	7.370×10^{46} hr (8.4×10^{43} yr)

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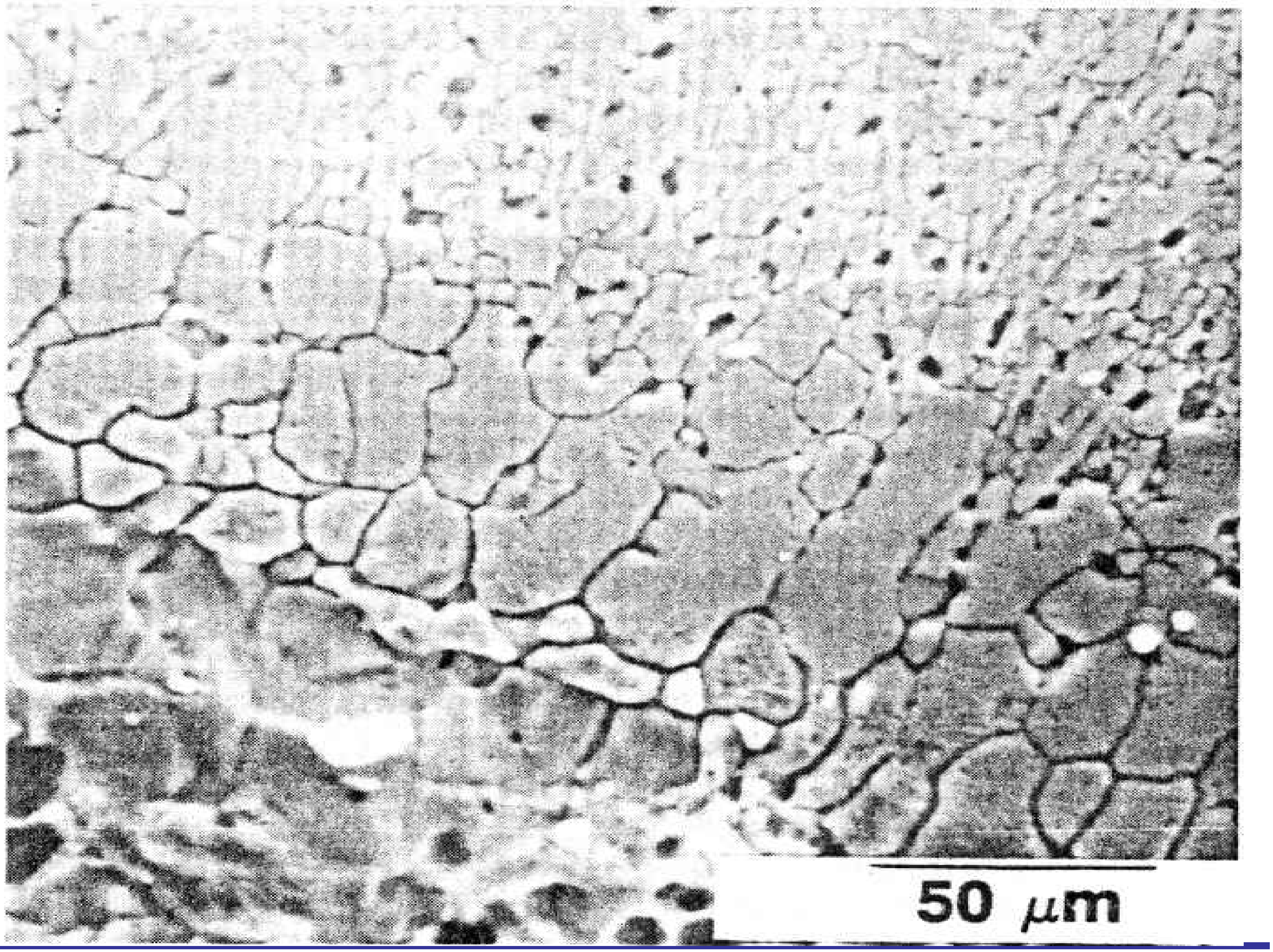
Recrystallization of the Ni electro-deposit starts at the Ni-Cu interface



Diffusion-induced 'Kirkendall' porosity occurs on the Cu side of the Cu/Ni interface

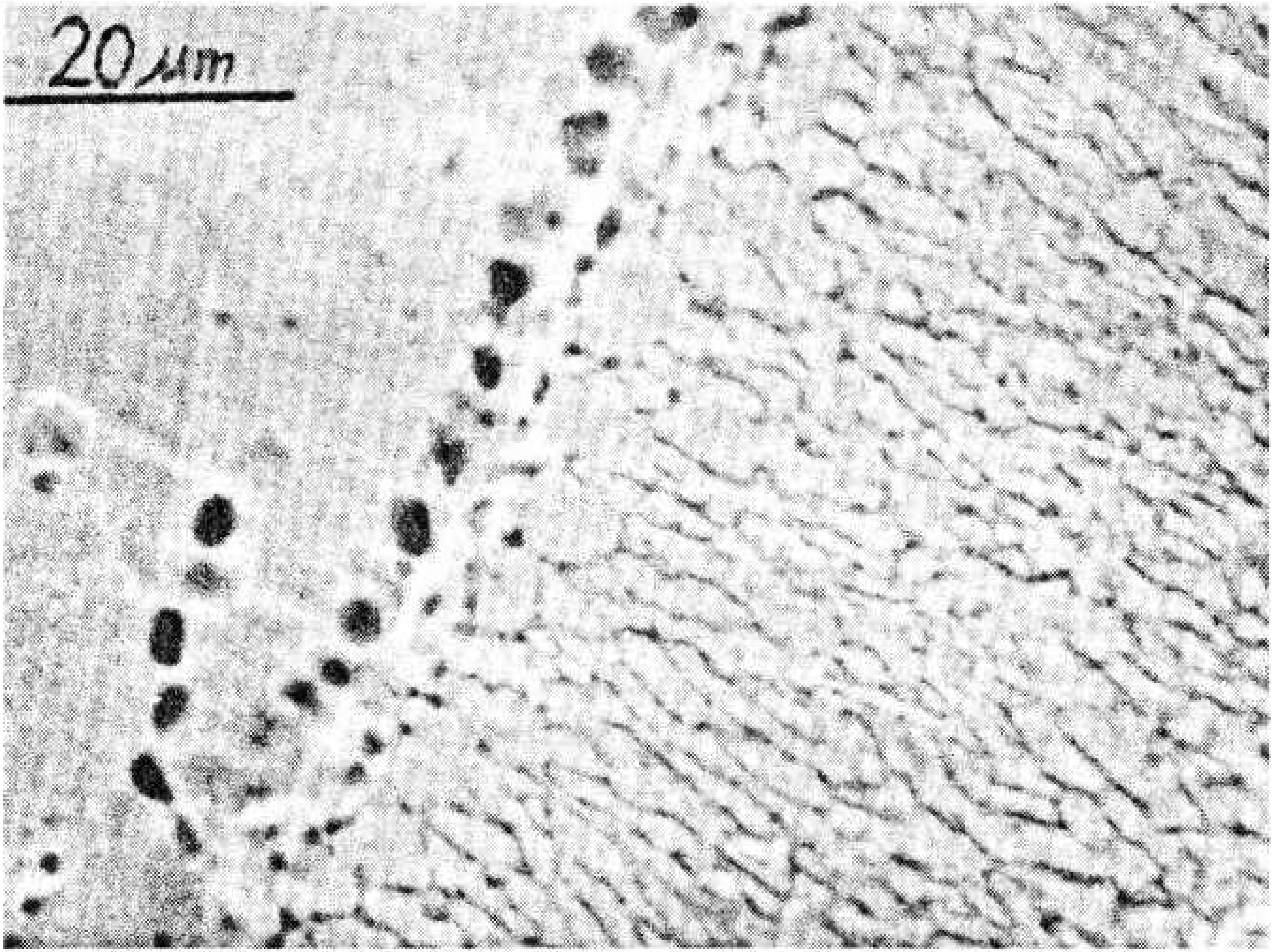


Fig. 6—TEM micrograph of as-plated Pd electrodeposit.

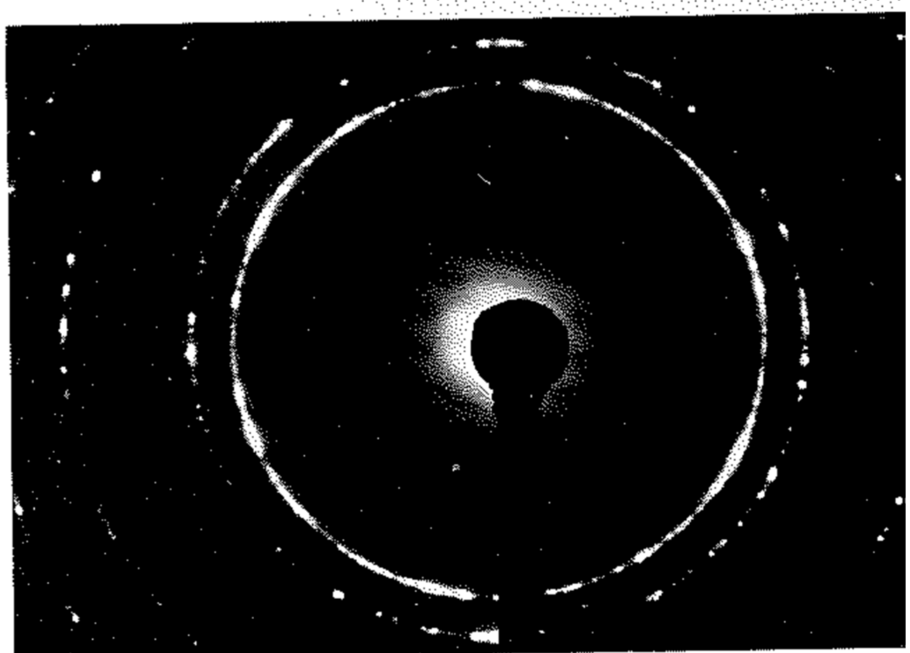


Fig. 7—SAD pattern obtained from region shown in Fig. 6.

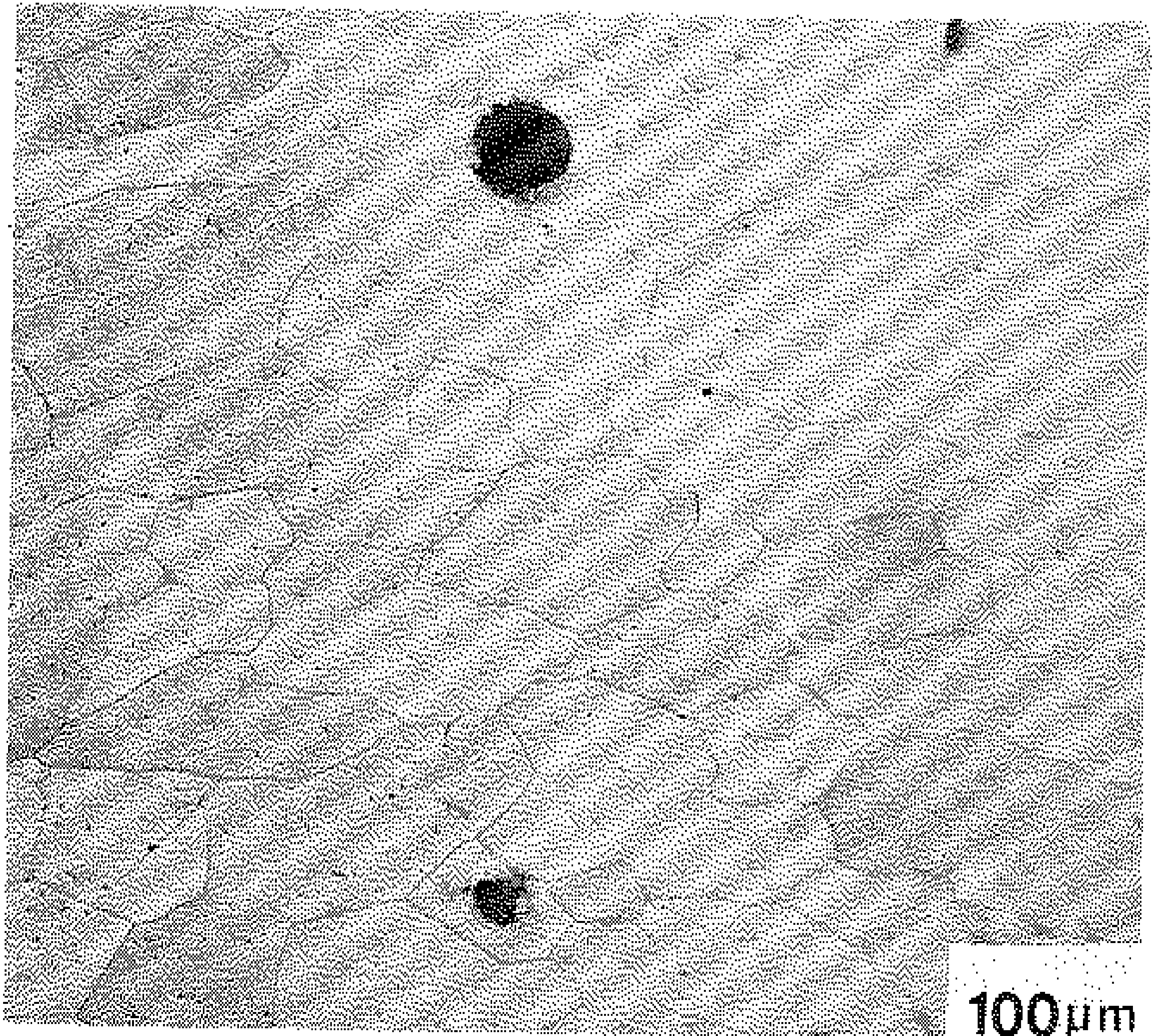


Fig. 5—Microstructure of wrought Pd.

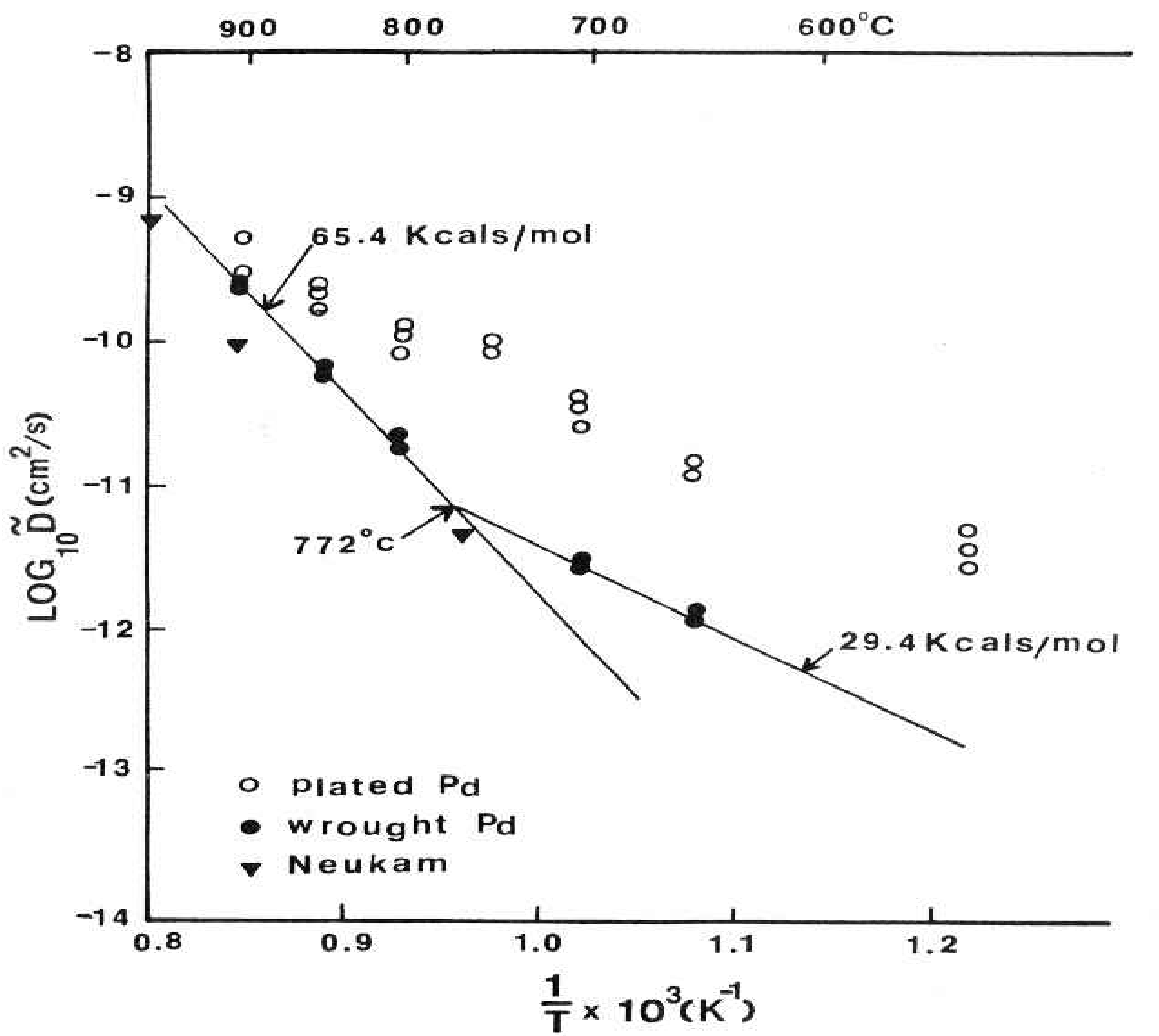


Fig. 2—Diffusivity of 50 atomic percent Pd coupled with Cu.

Experimental

- **All plating experiments were performed using commercial (Dipsol) plating baths.**
- **Steel samples, along with quartz crystals were used for analysis of the electrodeposits.**
- **In all corrosive tests, an aggressive 0.1 M Na_2SO_4 with dilute H_2SO_4 solution was used (pH 3.6) to simulate acid rain.**
- **A potentiostat was used to apply a potential and record the polarization curve.**
- **The open circuit potential was measured. Samples were run from the open circuit potential (-1080 mV_{SCE}) to various potentials and SEM images were taken.**

Theory of Electrochemical Quartz Crystal Microbalance

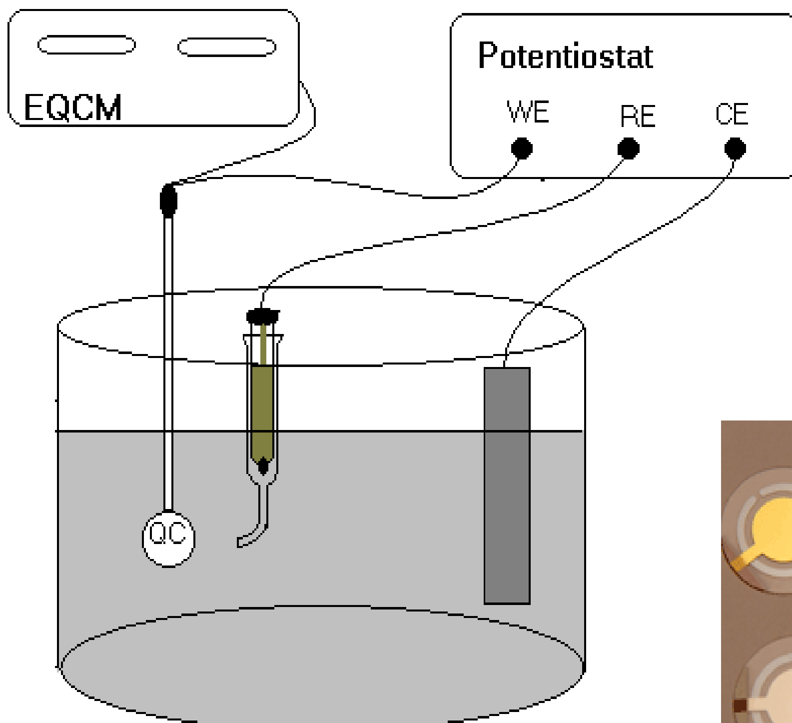
$$\Delta f = -K\Delta m$$

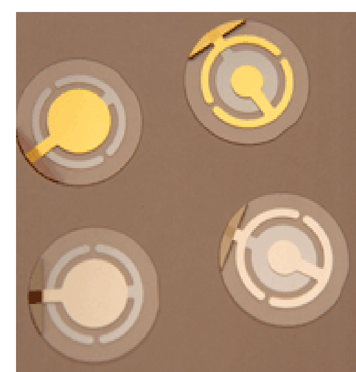
where :

Δf = change in resonant frequency

K = positive constant

Δm = change in mass





Reasons for Zinc-Nickel Research

- Replacement for zinc platings on steel for automobile body
  - Better in welding operations
  - Better in forming operations
  - Better paint performance
- Better corrosion resistance than Zn platings in Salt Spray Tests
  - Zinc-nickel deposits provide the cathodic protection of steel by the preferential dissolution of zinc
  - Susceptibility to Dezincification, Stress Corrosion Cracking or Passivation???

    These phenomena do not occur with Zn coatings.
- Thus, corrosion rate and lifetime under service conditions are difficult to predict.

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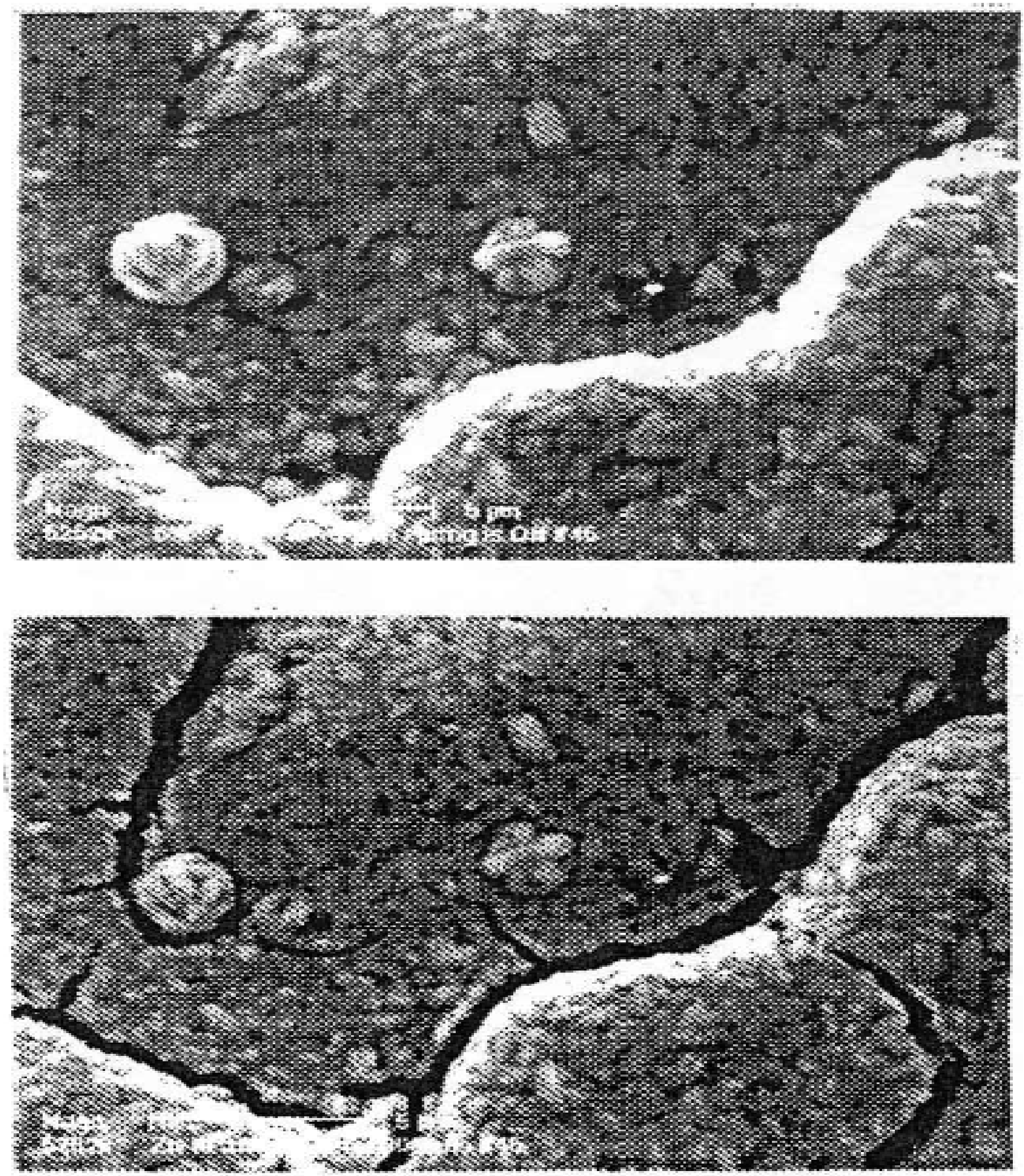
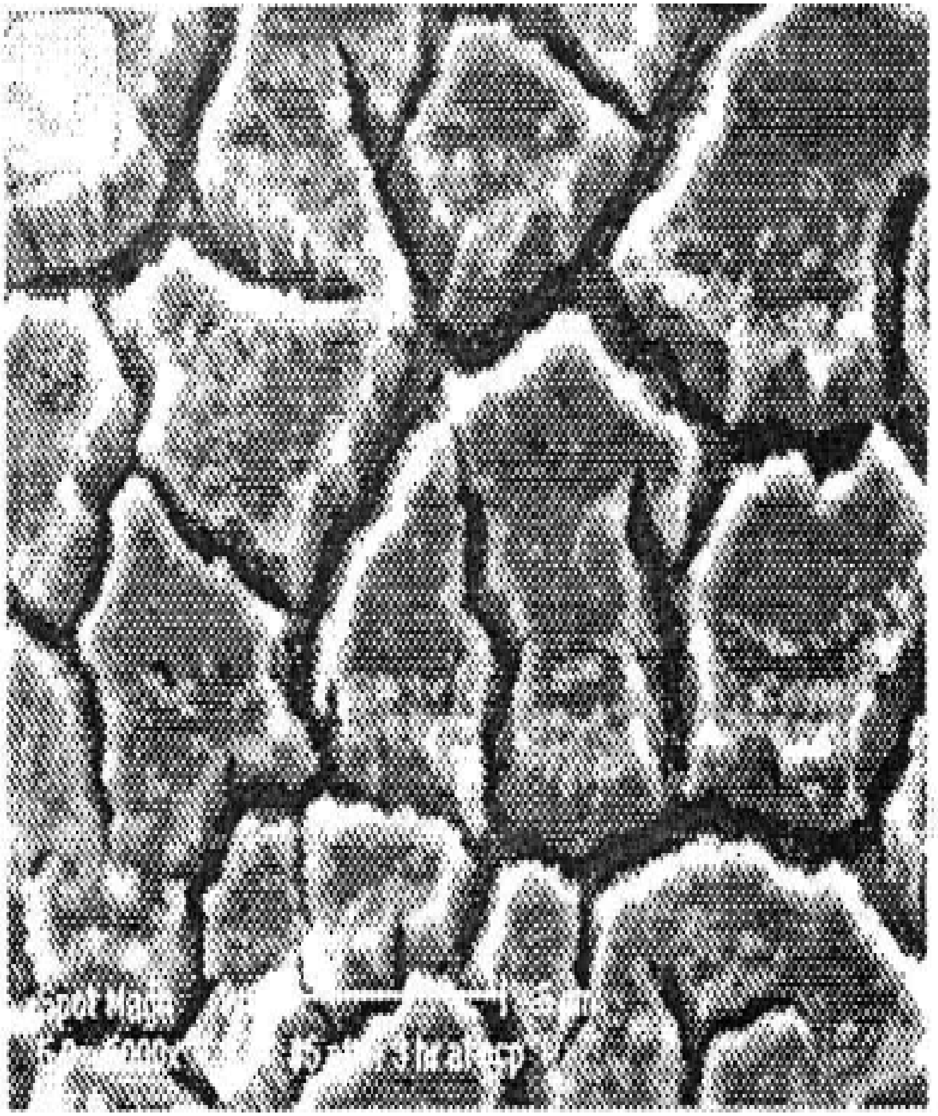
Zn-Ni

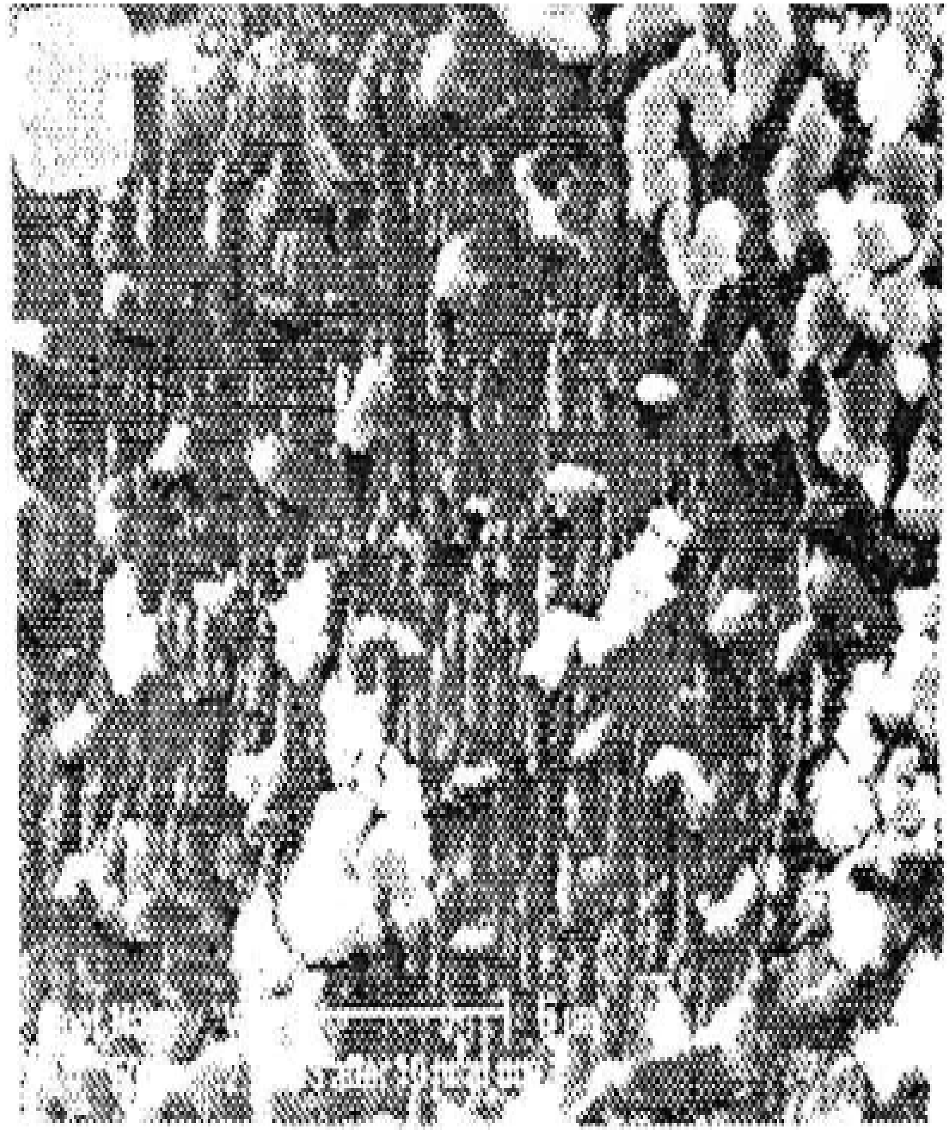


Electron micrographs of the surface of the Zn-Ni electrodeposit. Deposition current: 20 mA cm-2.

Upper image: after removal from the plating bath under current.

Lower image: same spot after 30 min in the corrosive bath.





Electron Micrographs of electrodeposited Zn-Ni alloy films after different corrosion times. (30 min image not shown) Left image: 3 h; Right image: 10 h

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Reasons for Tin-Zinc Research

- **Replacement for cadmium plating**
  - **Toxic**
  - **Carcinogenic**
- **Better corrosion resistance than cadmium platings**
  - **Tin-zinc deposits provide the cathodic protection of steel by the preferential dissolution of zinc**
- **Good solderability**
- **Bright matte finish**
- **Sn-Zn plating bath has favorable characteristics:**
  - **Non flammable**

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Objectives for Sn-Zn

- To develop a protective coating for steel surfaces that
  - can be prepared from an environmentally friendly bath and
  - does not require cadmium coating or any additional inhibiting surface treatment, such as chromating
- To understand corrosion mechanism associated with 70-30 (weight %) Sn-Zn alloy electrodeposits
  - leads to a lifetime prediction

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- Tin and zinc form separate phases, the metals are not miscible.
- In a 70/30 mixture of tin and zinc one has small zinc crystals dispersed in a matrix of tin crystals.
- Zinc dissolution will lead to the formation of voids and channels with a characteristic length $< 1\ \mu m$.
- This microstructure is the reason for the long lasting protective properties of the deposit.

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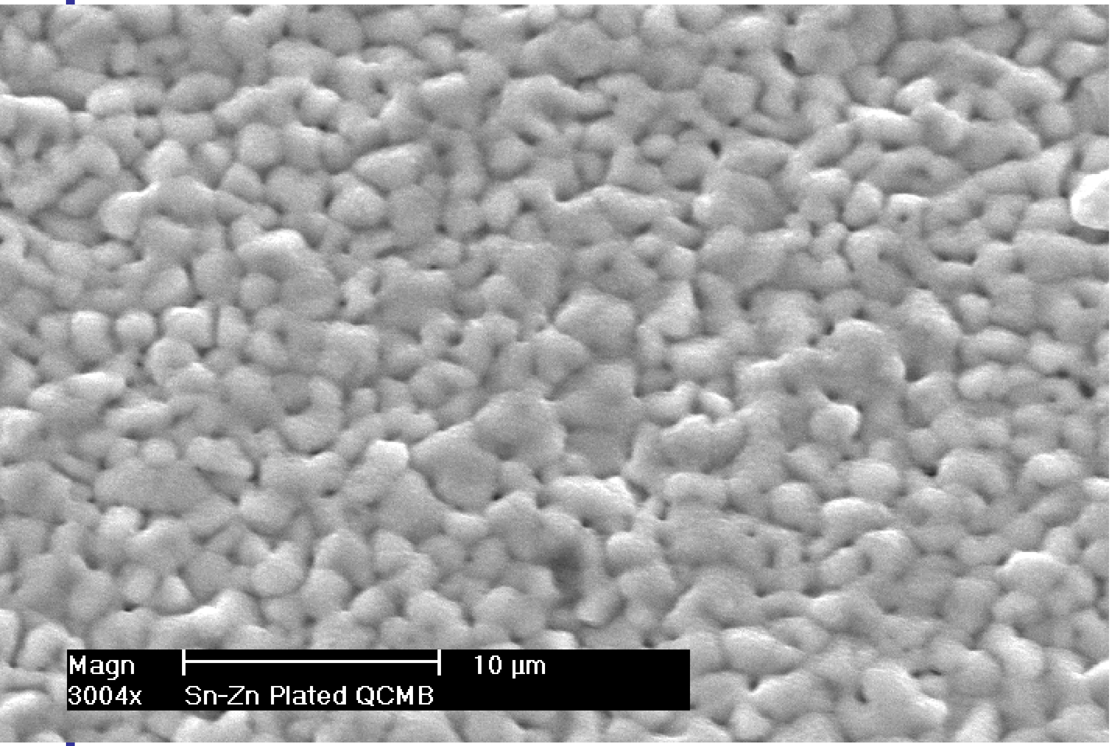
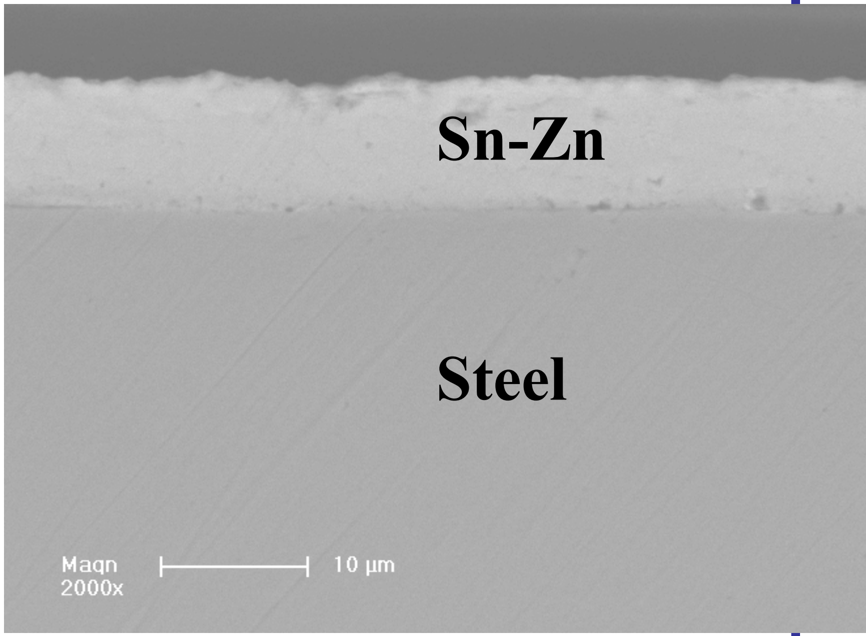
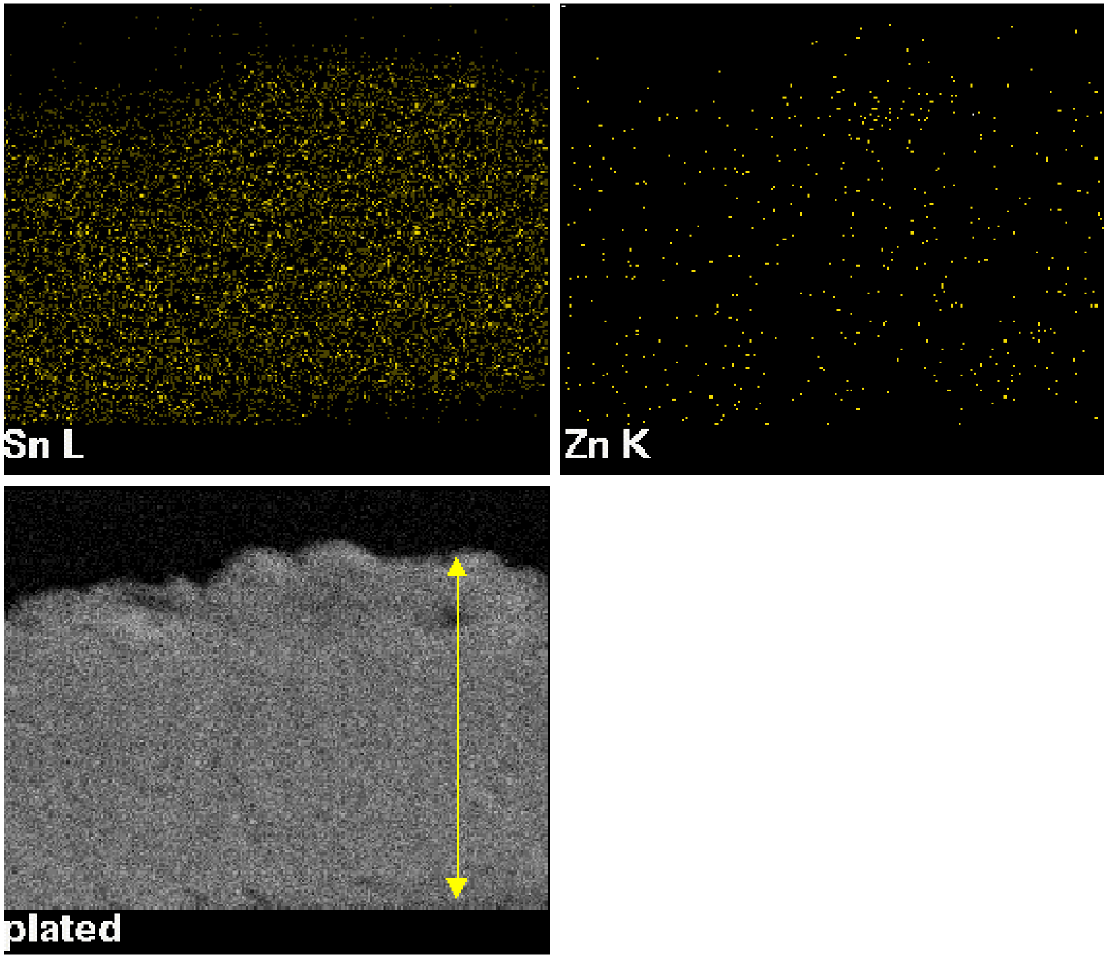
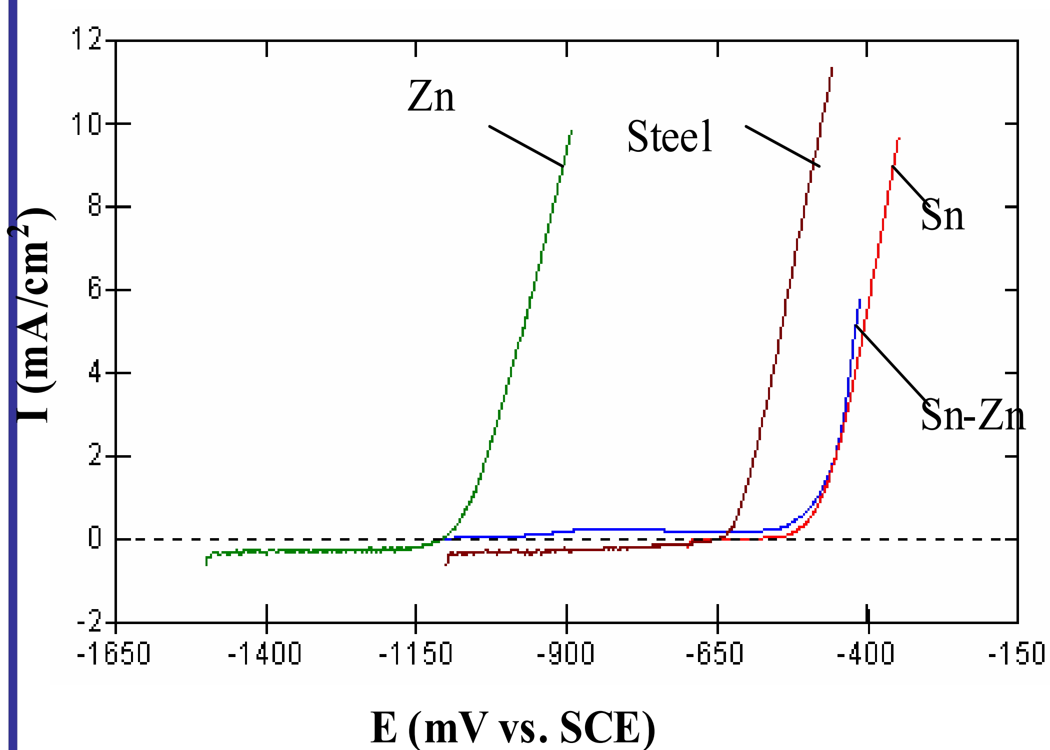
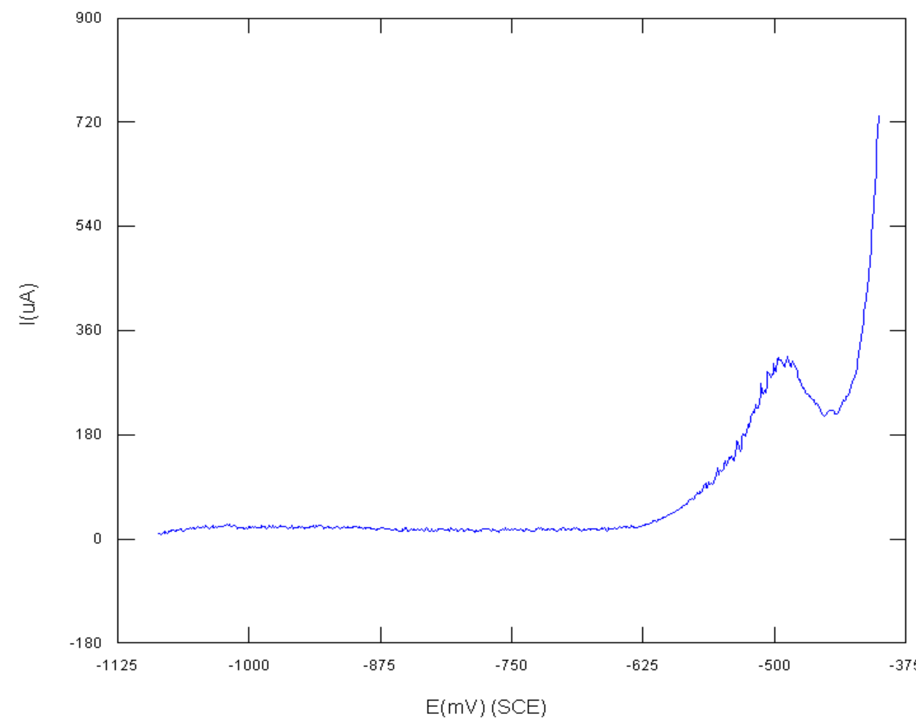

Magn
3004x
10 µm
Sn-Zn Plated QCMB


Sn-Zn
Steel
Magn
2000x
10 µm


Sn L
Zn K
plated





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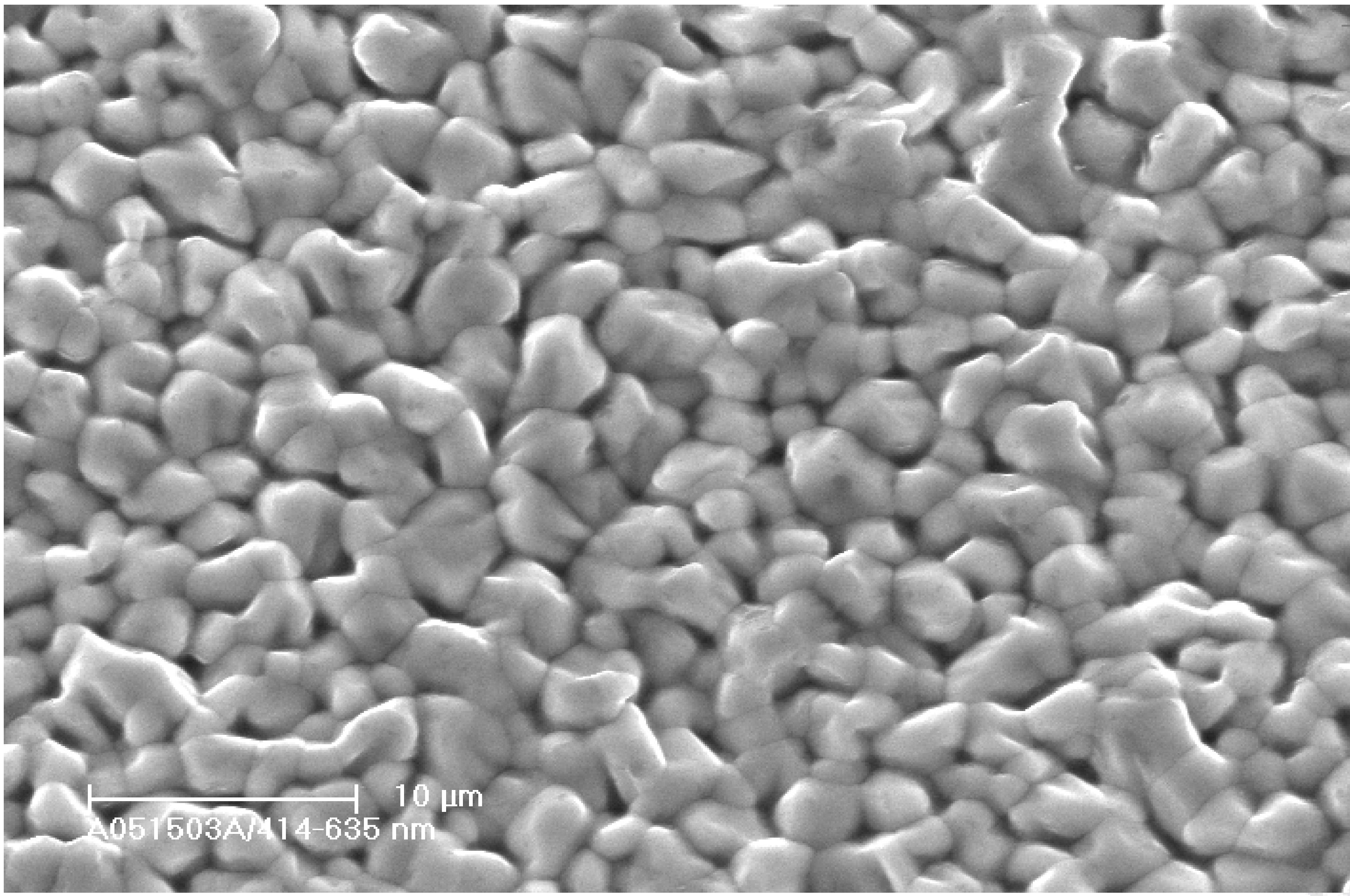

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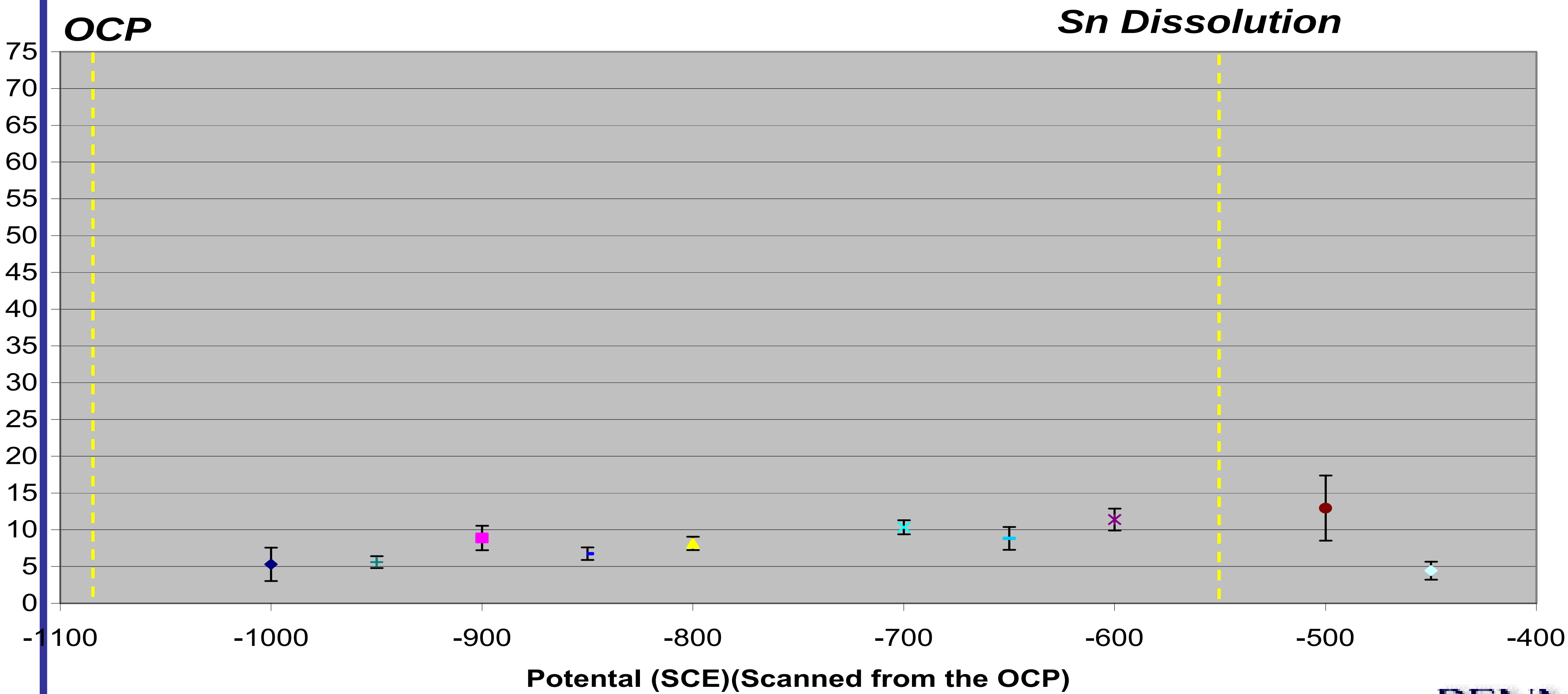
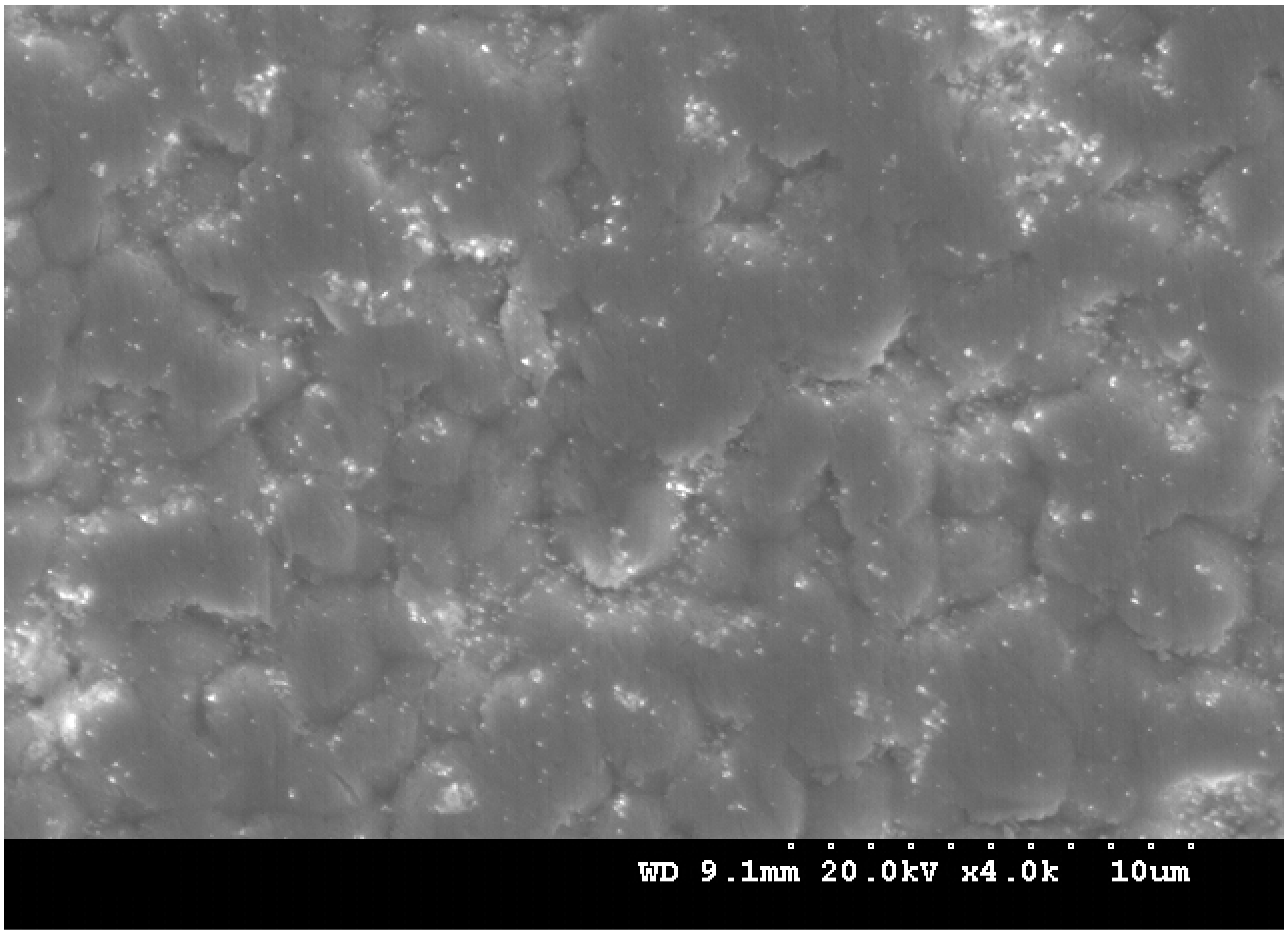
- The deposits consist of two interpenetrating networks:
- a rather coarse network of tin crystals and
- a finer network of zinc crystals
- During the potentiodynamic scan or during the corrosion period the zinc network disappears while the tin network persists

Surface Porosity vs Scanned Potental





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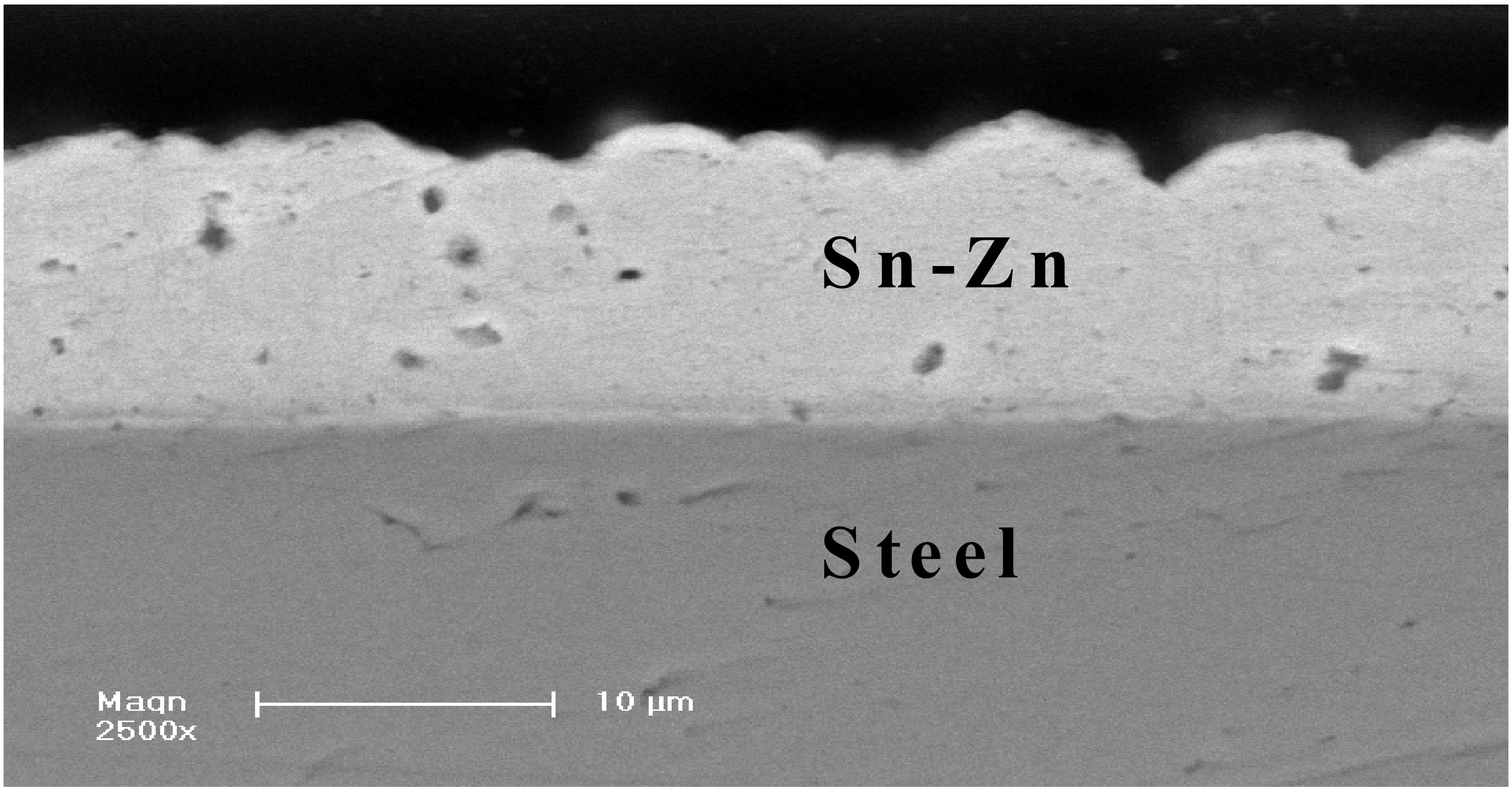

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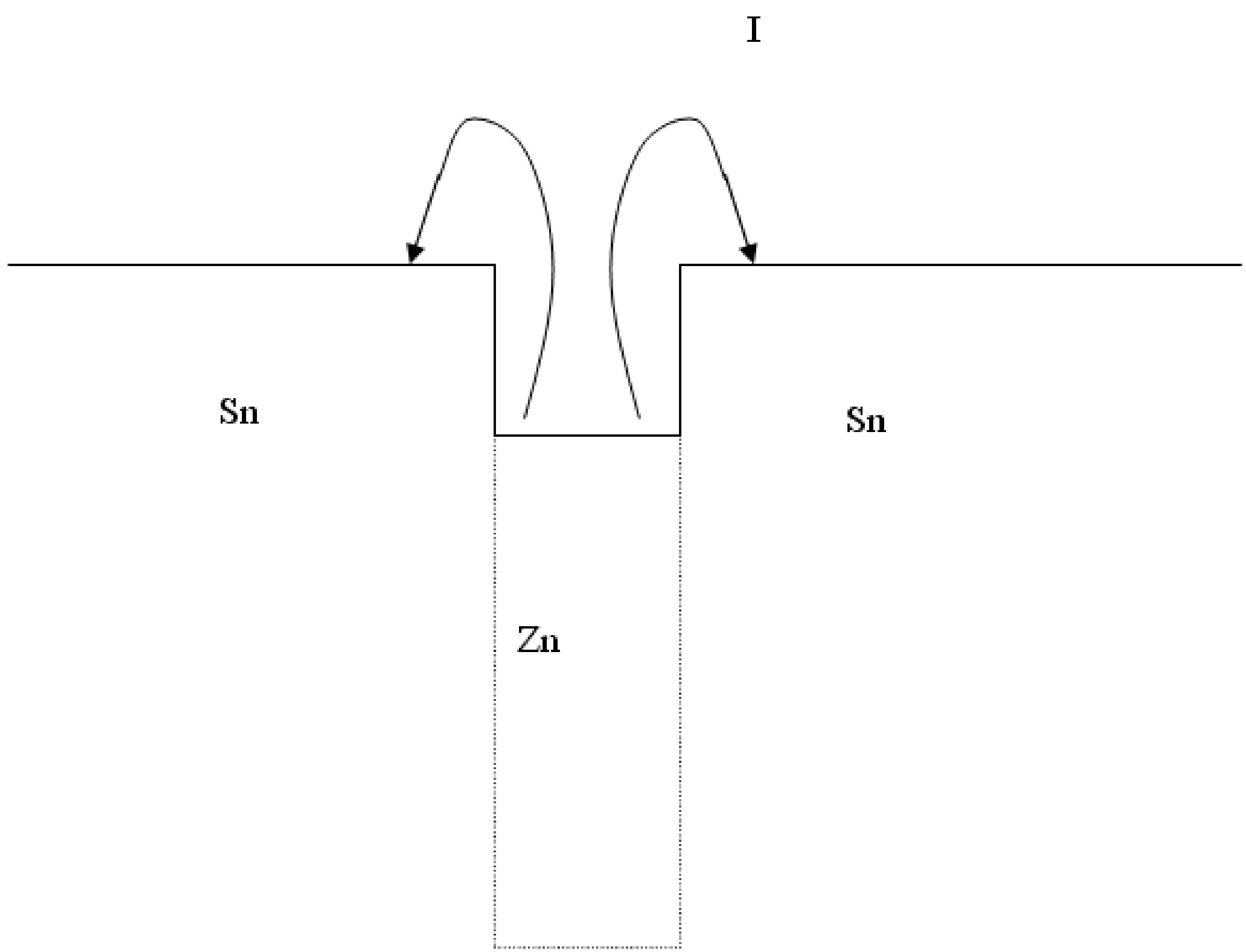
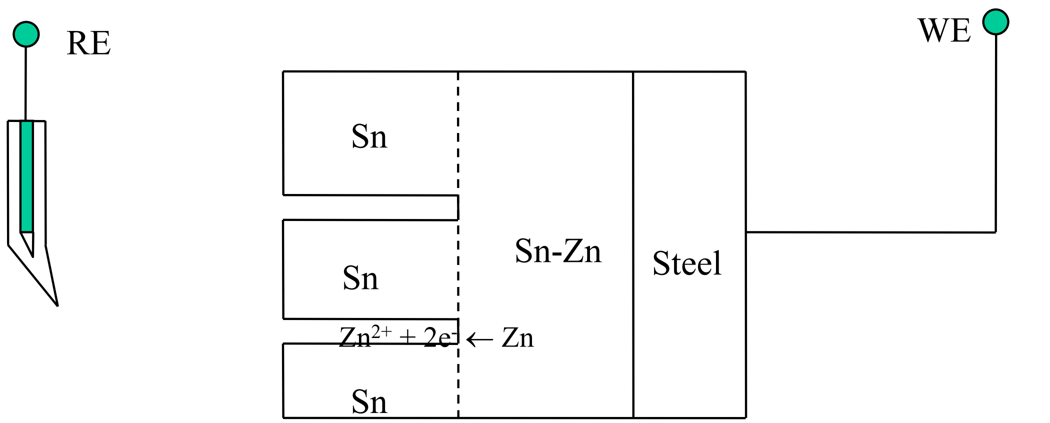
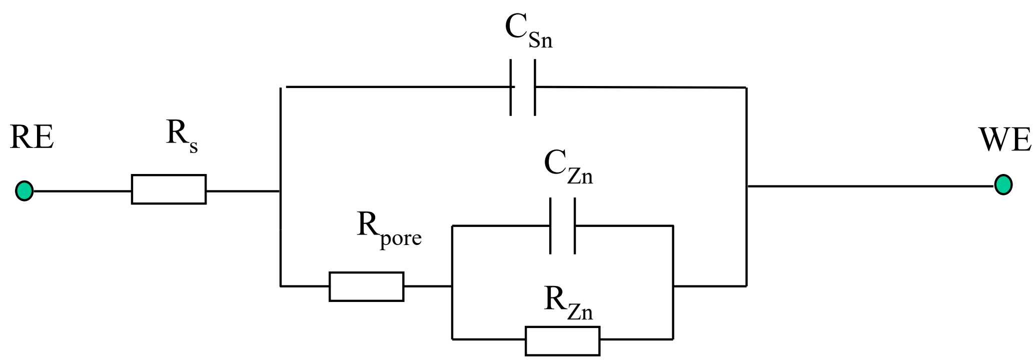
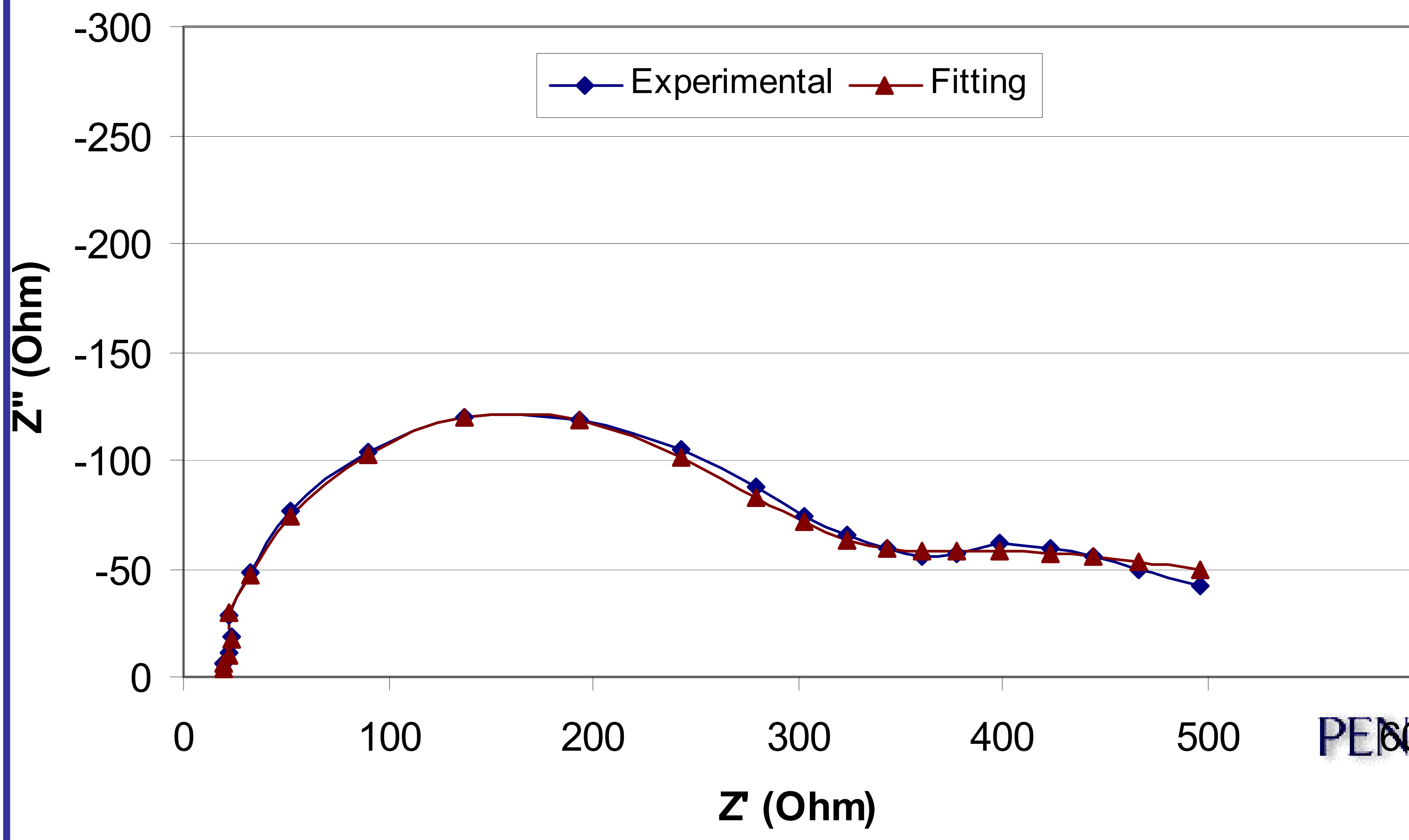
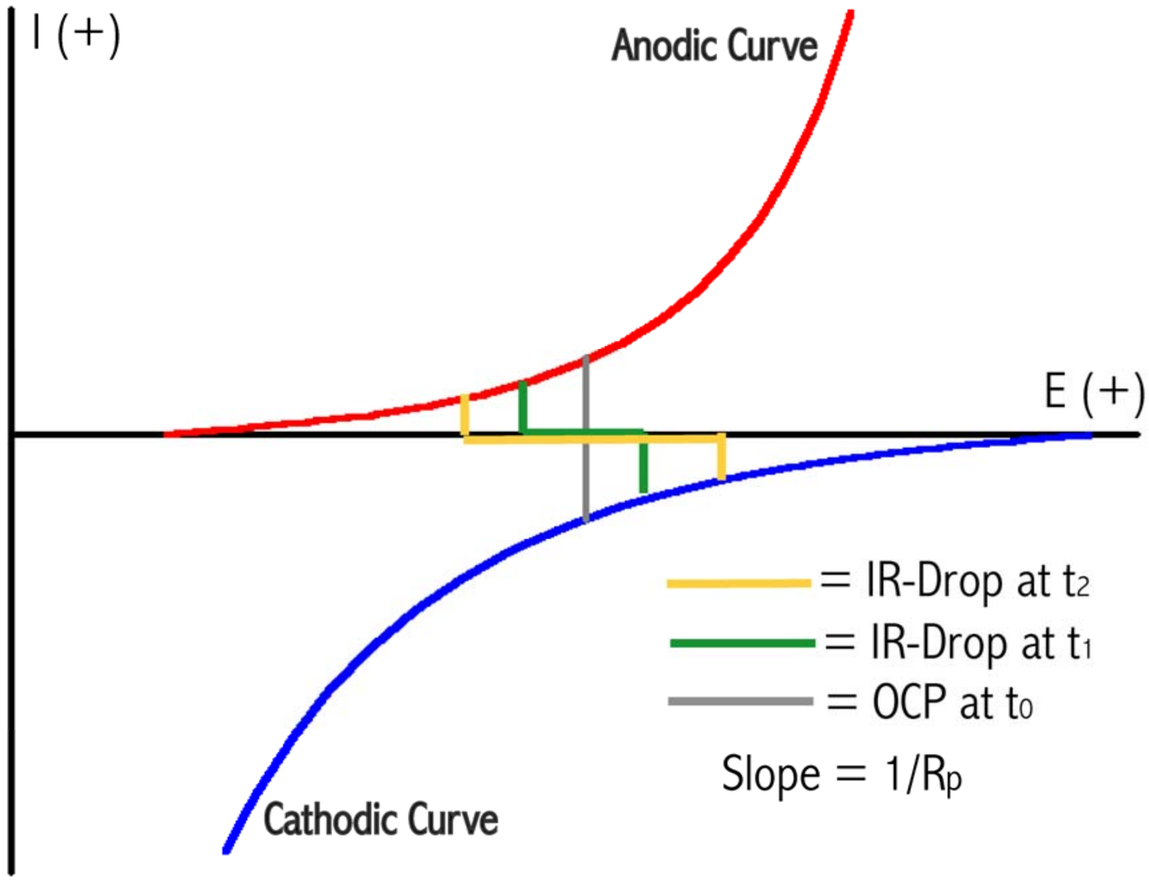

I
Sn
Sn
Zn


RE
WE
Sn
Sn
Sn
Sn-Zn
Steel
Zn2+ + 2e- ← Zn

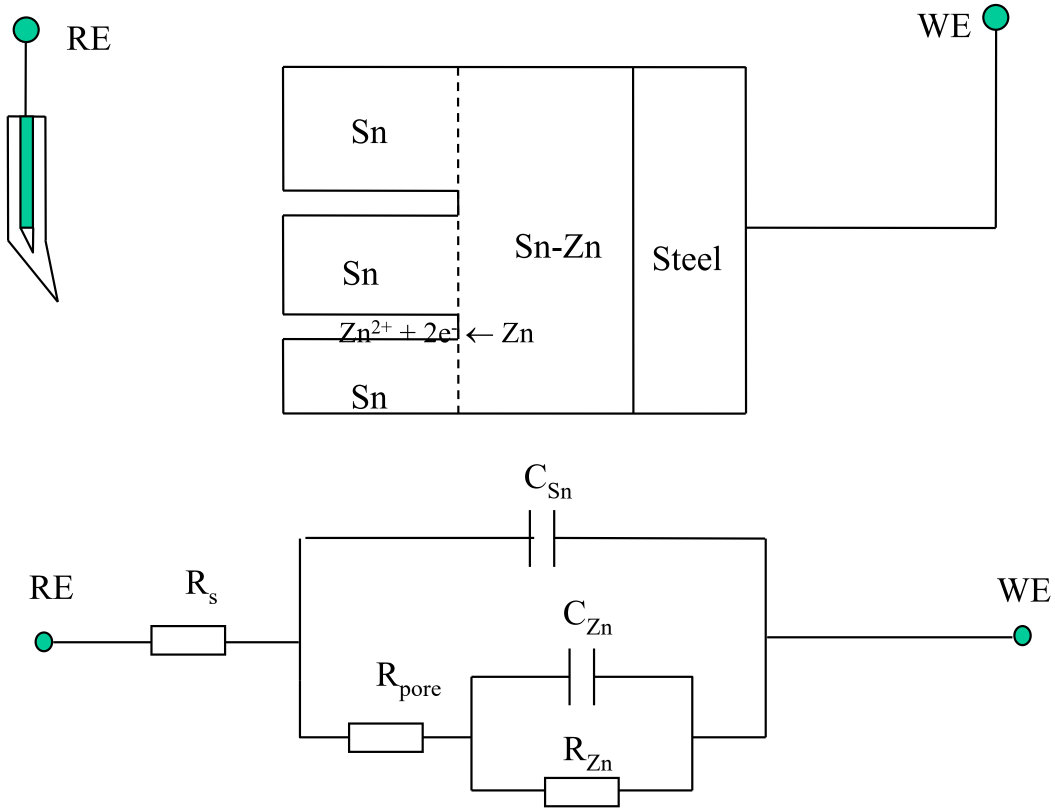

RE
Rs
CSn
CZn
Rpore
RZn
WE



Experimental
Fitting
-300
-250
-200
-150
-100
-50
0
Z" (Ohm)
0
100
200
300
400
500
600
Z' (Ohm)


I (+)
Anodic Curve
E (+)
= IR-Drop at t2
= IR-Drop at t1
= OCP at t0
Slope = 1/Rp
Cathodic Curve

Time (hours)	R_s	R_{pore}	R_{zn}	C_{sn}	α (Sn)	C_{zn}	α (Zn)
2	19.41	157.2	145.6	2.041E-5	0.911	8.21E-3	0.577
4	19.16	170.9	199.2	1.940E-5	0.919	6.56E-3	0.519
7	19.15	239.2	344	1.853E-5	0.927	2.97E-3	0.387
10	18.83	460.1	229	1.922E-5	0.922	1.337E-3	0.595
20	18.68	1858	5606	2.333E-5	0.901	7.222E-5	0.192
24	18.31	20679	9657	2.825E-5	0.879	4.176E-4	0.795
28	18.00	335959	12645	3.053E-5	0.872	3.828E-4	0.935



RE
WE
Sn
Sn
Sn
Sn-Zn
Steel
$Zn^{2+} + 2e^- \leftarrow Zn$
RE
R_s
C_{Sn}
C_{Zn}
R_{pore}
R_{Zn}
WE

Acknowledgements

- Dipsol of America
- AESF Project 109
- Project 109 Committee Members
  - Dr. James Lindsay
  - Dr. George DiBari
  - Mr. Harry J. Litsch

DIPSOL

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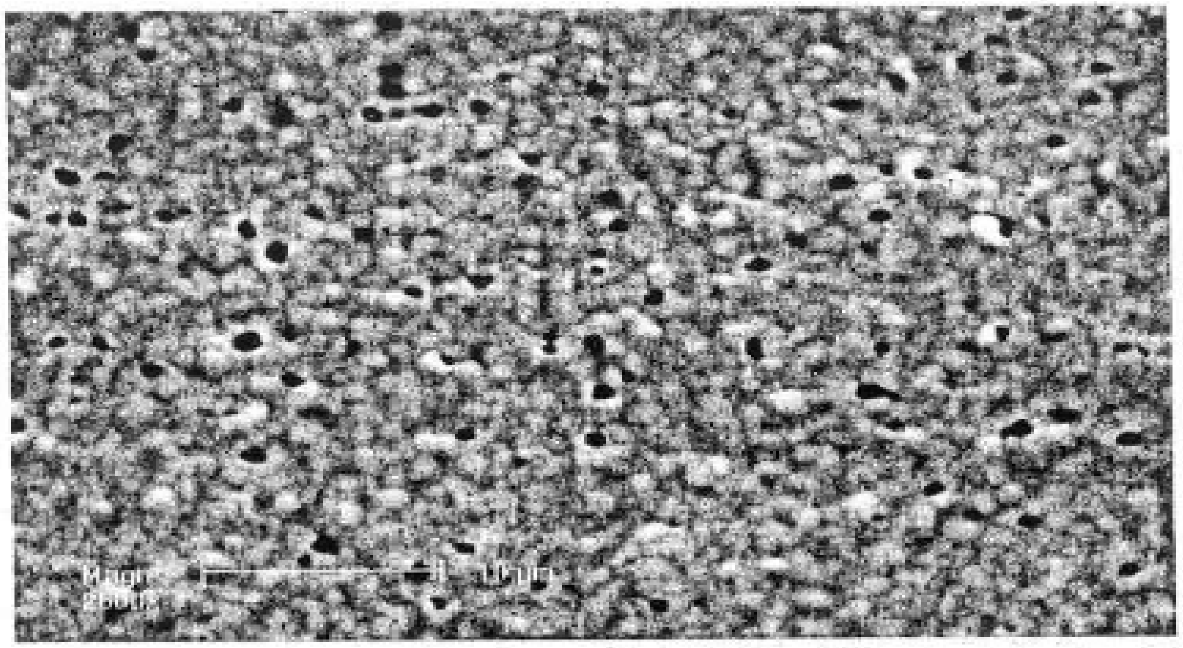

Fig. 2—SEM image of the electroplated 70Sn-30Zn deposit after 24 hours of corrosion at OCP in 0.1M Na_2SO_4 (pH 3.6) solution.

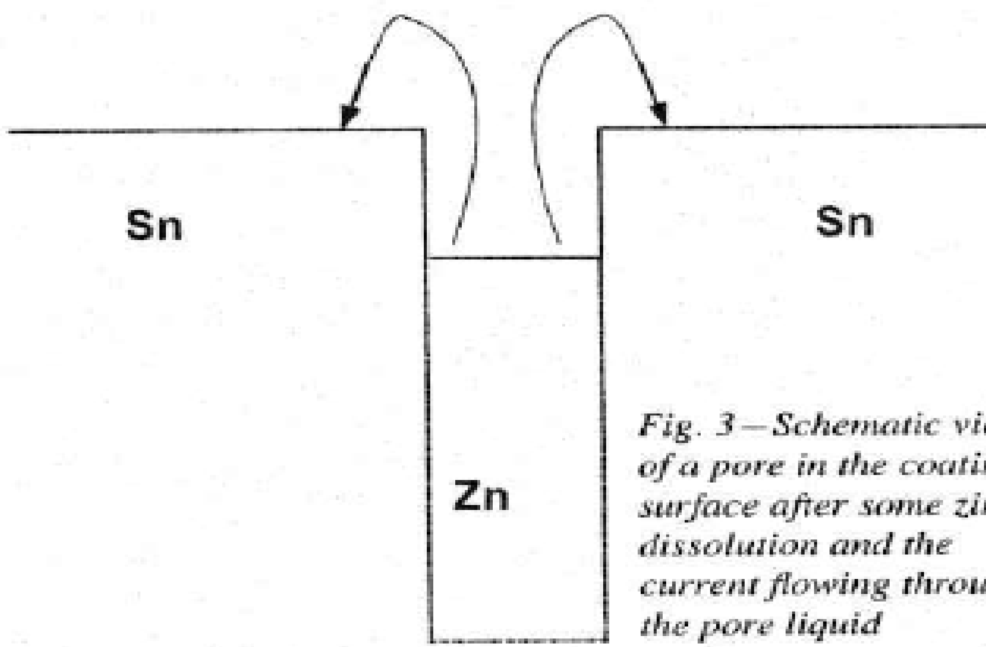

Fig. 3—Schematic view of a pore in the coating surface after some zinc dissolution and the current flowing through the pore liquid

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