DECLARATION OF JUNE ANN MUNFORD

1. My name is June Ann Munford. I am over the age of 18, have personal knowledge of the facts set forth herein, and am competent to testify to the same.

2. I earned a Master of Library and Information Science (MLIS) from the University of Wisconsin-Milwaukee in 2009. I have over ten years of experience in the library/information science field. Beginning in 2004, I have served in various positions in the public library sector including Assistant Librarian, Youth Services Librarian and Library Director. I have attached my Curriculum Vitae as Appendix CV.

3. During my career in the library profession, I have been responsible for materials acquisition for multiple libraries. In that position, I have cataloged, purchased and processed incoming library works. That includes purchasing materials directly from vendors, recording publishing data from the material in question, creating detailed material records for library catalogs and physically preparing that material for circulation. In addition to my experience in acquisitions, I was also responsible for analyzing large collections of library materials, tailoring library records for optimal catalog

search performance and creating lending agreements between libraries during my time as a Library Director.

4. I am fully familiar with the catalog record creation process in the library sector. In preparing a material for public availability, a library catalog record describing that material would be created. These records are typically written in Machine Readable Catalog (herein referred to as "MARC") code and contain information such as a physical description of the material, metadata from the material's publisher, and date of library acquisition. In particular, the 008 field of the MARC record is reserved for denoting the date of creation of the library record itself. As this typically occurs during the process of preparing materials for public access, it is my experience that an item's MARC record indicates the date of an item's public availability.

5. Typically, in creating a MARC record, a librarian would gather various bits of metadata such as book title, publisher and subject headings among others and assign each value to a relevant numerical field. For example, a book's physical description is tracked in field 300 while title/attribution is tracked in field 245. The 008 field of the MARC record is reserved for denoting the creation of the library record itself. As this is the only date reflecting the inclusion of said materials within the library's collection, it is my experience

that an item's 008 field accurately indicates the date of an item's public availability.

6. I have reviewed Exhibit SOLUS-1013, "Role of Overpotential on Texture, Morphology and Ductility of Electrodeposited Copper Foils for Printed Circuit Board Applications" by Xingpu Ye, et al as published in *Journal of the Electrochemical Society*, June 1992.

7. Attached hereto as Appendix YE01 is a true and correct copy of the MARC record for *Journal of the Electrochemical Society* as held by the Carnegie Library of Pittsburgh. I secured this record myself from the library's public catalog. The MARC record contained within Appendix YE01 accurately describes the title, author, publisher, and ISSN number of *Journal of the Electrochemical Society.* The 'Lib Has' field of this record visible on page 3 indicates this collection includes the June 1992 edition of *Journal of the Electrochemical Society* containing "Role of Overpotential on Texture, Morphology and Ductility of Electrodeposited Copper Foils for Printed Circuit Board Applications".

8. Attached hereto as Appendix YE02 is a true and correct copy of "Role of Overpotential on Texture, Morphology and Ductility of Electrodeposited

Copper Foils for Printed Circuit Board Applications" as published in *Journal of the Electrochemical Society* as held by the Carnegie Library of Pittsburgh. I secured these scans myself from the library's collection. In comparing Exhibit SOLUS-1013 to Appendix YE02, it is my determination that Exhibit SOLUS-1013 is a true and correct copy of "Role of Overpotential on Texture, Morphology and Ductility of Electrodeposited Copper Foils for Printed Circuit Board Applications" by Xingpu Ye, et al as published in *Journal of the Electrochemical Society* June 1992.

9. The 008 field of the MARC record in Appendix YE01 indicates the date of record creation. The 008 field of Appendix YE01 indicates the Carnegie Library of Pittsburgh first acquired this journal as of Subscription Date and held the journal in perpetuity until 2012. Considering this information, it is my determination that *Journal of the Electrochemical Society* June 1992 and therefore "Role of Overpotential on Texture, Morphology and Ductility of Electrodeposited Copper Foils for Printed Circuit Board Applications" was made available to the public shortly after its initial release in June 1992.

10. I have reviewed Exhibit SOLUS-1018, "Effects of Organic Additives on Residual Stress and Surface Roughness of Electroplated Copper for Flexible

PCB" by Kim, et al. as published in *Corrosion Science and Technology*, August 2007.

11. Attached hereto as Appendix KIM01 is a true and correct copy of the MARC record for *Corrosion Science and Technology* as held by the Library of Congress. I secured this record myself from the library's public catalog. The MARC record contained within Appendix KIM01 accurately describes the title, author, publisher, and ISSN number of *Corrosion Science and Technology.* The 'Item Availability' field of this record visible on page 3 indicates this collection includes the August 2007 edition of *Corrosion Science and Technology* containing "Effects of Organic Additives on Residual Stress and Surface Roughness of Electroplated Copper for Flexible PCB". In comparing Exhibit SOLUS-1018 to Appendix KIM01, it is my determination that Exhibit SOLUS-1018 is a true and correct copy of "Effects of Organic Additives on Residual Stress and Surface Roughness of Electroplated Copper for Flexible PCB" by Kim, et al. as published in *Corrosion Science and Technology* August 2007.

12. The 008 field of the MARC record in Appendix KIM01 indicates the date of record creation. The 008 field of Appendix KIM01 indicates the Library of Congress first acquired this journal as of February 13, 2008 and held the

journal in perpetuity until 2011. Considering this information, it is my determination that *Corrosion Science and Technology* August 2007 and therefore "Effects of Organic Additives on Residual Stress and Surface Roughness of Electroplated Copper for Flexible PCB" was made available to the public shortly after its initial release in August 2007.

13. I have been retained on behalf of the Petitioner to provide assistance in the above-illustrated matter in establishing the authenticity and public availability of the documents discussed in this declaration. I am being compensated for my services in this matter at the rate of $200.00 per hour plus reasonable expenses. My statements are objective, and my compensation does not depend on the outcome of this matter.

14. I declare under penalty of perjury that the foregoing is true and correct. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Dated: 10/3/2024



June Ann Munford

APPENDIX CV

June A. Munford
Curriculum Vitae

Education

University of Wisconsin-Milwaukee - MS, Library & Information Science, 2009
Milwaukee, WI

- Coursework included cataloging, metadata, data analysis, library systems, management strategies and collection development.
- Specialized in library advocacy, cataloging and public administration.

Grand Valley State University - BA, English Language & Literature, 2008
Allendale, MI

- Coursework included linguistics, documentation and literary analysis.
- Minor in political science with a focus in local-level economics and government.

Professional Experience

Researcher / Expert Witness, October 2017 – present
Freelance ● Pittsburgh, Pennsylvania & Grand Rapids, Michigan

- Material authentication and public accessibility determination. Declarations of authenticity and/or public accessibility provided upon research completion. Experienced with appeals and deposition process.

- Research provided on topics of public library operations, material publication history, digital database services and legacy web resources.

- Past clients include Alston & Bird, Arnold & Porter, Baker Botts, Fish & Richardson, Erise IP, Irell & Manella, O'Melveny & Myers, Perkins-Coie, Pillsbury Winthrop Shaw Pittman and Slayden Grubert Beard.

Library Director, February 2013 - March 2015
Dowagiac District Library ● Dowagiac, Michigan

- Executive administrator of the Dowagiac District Library. Located in

Southwest Michigan, this library has a service area of 13,000, an annual operating budget of over $400,000 and total assets of approximately $1,300,000.

● Developed careful budgeting guidelines to produce a 15% surplus during the 2013-2014 & 2014-2015 fiscal years while being audited.

● Using this budget surplus, oversaw significant library investments including the purchase of property for a future building site, demolition of existing buildings and building renovation projects on the current facility.

● Led the organization and digitization of the library's archival records.

● Served as the public representative for the library, developing business relationships with local school, museum and tribal government entities.

● Developed an objective-based analysis system for measuring library services - including a full collection analysis of the library's 50,000+ circulating items and their records.

November 2010 - January 2013
Librarian & Branch Manager, Anchorage Public Library ● Anchorage, Alaska

● Headed the 2013 Anchorage Reads community reading campaign including event planning, staging public performances and creating marketing materials for mass distribution.

● Co-led the social media department of the library's marketing team, drafting social media guidelines, creating original content and instituting long-term planning via content calendars.

● Developed business relationships with The Boys & Girls Club, Anchorage School District and the US Army to establish summer reading programs for children.

June 2004 - September 2005, September 2006 - October 2013
Library Assistant, Hart Area Public Library
Hart, MI

● Responsible for verifying imported MARC records and original MARC

cataloging for the local-level collection as well as the Michigan Electronic Library.

● Handled OCLC Worldcat interlibrary loan requests & fulfillment via ongoing communication with lending libraries.

Professional Involvement

Alaska Library Association - Anchorage Chapter
- Treasurer, 2012

Library Of Michigan
- Level VII Certification, 2008
- Level II Certification, 2013

Michigan Library Association Annual Conference 2014
- New Directors Conference Panel Member

Southwest Michigan Library Cooperative
- Represented the Dowagiac District Library, 2013-2015

Professional Development

Library Of Michigan Beginning Workshop, May 2008
Petoskey, MI
- Received training in cataloging, local history, collection management, children's literacy and reference service.

Public Library Association Intensive Library Management Training, October 2011
Nashville, TN
- Attended a five-day workshop focused on strategic planning, staff management, statistical analysis, collections and cataloging theory.

Alaska Library Association Annual Conference 2012 - Fairbanks, February 2012
Fairbanks, AK
- Attended seminars on EBSCO advanced search methods, budgeting, cataloging, database usage and marketing.

Depositions

2019 ● Fish & Richardson

Apple v. Qualcomm (IPR2018-001281, 39521-00421IP, IPR2018-01282 and 39521-00421IP2)

2019 ● Erise IP

Implicit, LLC v. Netscout Systems, Inc (Civil Action No. 2:18-cv-53-JRG)

2019 ● Perkins-Coie

Adobe Inc. v. RAH Color Technologies LLC (Cases IPR2019-00627, IPR2019-00628, IPR2019-00629 and IPR2019-00646)

2020 ● O'Melveny & Myers

Maxell, Ltd. v. Apple Inc. (Case No. 5:19-cv-00036-RWS)

2021 ● Pillsbury Winthrop Shaw Pittman LLP

Intel v. SRC (IPR2020-1449)

2022 ● Perkins-Coie

Realtek v. Future Link (IPR2021-01182)

2023 ● Fish & Richardson

Neuroderm Ltd. v. Abbvie, Inc (Case No. PGR2022-00040)

2023 ● Fish & Richardson

Nearmap US Inc. v. Pictometry International Corp. (IPR2022-00735)

2023 ● Fish & Richardson

Samsung Electronics v. MemoryWeb LLC (Case No. 39843-0136PS1)

2023 ● Pillsbury Winthrop Shaw Whitman LLP

Gravel Rating Systems v. Costco Wholesale Corp. (Civil Action No. 4:21-cv-149-ALM)

2024 ● Willkie-Farr

Netflix, Inc. v. VideoLabs. Inc. (IPR2023-00628)

Limited Case and Clientele History

Alston & Bird

- Ericsson

  v. Collision Communications (IPR2022-01233)

- Nokia

  v. Neptune Subsea, Xtera (Case No. 1:17-cv-01876)

- Universal Electronics Inc

  v. Roku Inc (IPR2022-00818)

Arnold & Porter

- Ivantis

  v. Glaukos (Case No. 8:18-cv-00620)

- Samsung

  v. Jawbone (Case No. 2:21-cv-00186)

Benesch Friedlander Coplan & Aronoff

- Voyis

  v. Cathx (Case No. 5:21-cv-00077-RWS)

Deschert LLP

- Smaxtec Animal Care

  v. ST Reproductive Technologies, LLC (IPR2024-00885)

Erise I.P.

- Apple

  v. Ericsson Inc. (IPR2022-00715)

  v. Future Link Systems (IPRs 6317804, 6622108, 6807505, and 7917680)

  v. INVT (Case No. 20-1881)

  v. Navblazer LLC (IPR2020-01253)

  v. Qualcomm (IPR2018-001281, 39521-00421IP, IPR2018-01282, 39521-00421IP2)

  v. Quest Nettech Corp (Case No. 2:19-cv-00118-JRG)

  v. Telefonaktiebolaget LM Ericsson (IPR2022-00275)

  v. Theta IP, LLC (IPR2024-00818)

- Fanduel

  v. CGT (Case No. 19-1393)

- Garmin

  v. Phillips North America LLC (Case No. 2:19-cv-6301-AB-KS)

- Netscout
    - v. Longhorn HD LLC (Case No. 2:20-cv-00349)
    - v. Implicit, LLC (Civil Action No. 2:18-cv-53-JRG)

- Sony Interactive Entertainment LLC
    - v. Bot M8 LLC (IPR2020-01288)
    - v. Infernal Technology LLC (Case No. 2:19-CV-00248-JRG)

- Unified Patents
    - v. GE Video Compression (Civil Action No. 2:19-cv-248)

Fish & Richardson

- Apple
    - v. AliveCor (3:21-cv-03958)
    - v. LBS Innovations (Case No. 2:19-cv-00119-JRG-RSP)
    - v. Koss Corporation (IPR2021-00305)
    - v. Masimo (IPR 50095-0012IP1, 50095-0012IP2, 50095-0013IP1, 50095-0013IP2, 50095-0006IP1, 50095-0135IP1)
    - v. Neonode (Case No. 21-cv-08872-EMC)
    - v. Qualcomm (IPR2018-001281, 39521-00421IP, IPR2018-01282, 39521-00421IP2)

- Dell
    - v. Neo Wireless (IPR2022-00616)

- Dish Network
    - v. Entropic Communications, LLC (Case No. 2:2023-CV-01043)

v. Realtime Adaptive Streaming (Case No. 1:17-CV-02097-RBJ)

v. TQ Delta LLC (Case No. 18-1798)

- Evapco Dry Cooling

  v. SPG Dry Cooling (IPR2021-00688)

- Genetec

  v. Sensormatic Electronics (Case No. 1:20-CV-00760)

- Huawei

  v. Bell Northern Research LLC (IPR2019-01174)

- Kianxis

  v. Blue Yonder (Case No. 3:20-cv-03636)

- LG Electronics

  v. Bell Northern Research LLC (Case No. 3:18-cv-2864-CAB-BLM)

- Metaswitch

  v. Sonus Networks (IPR2018-01719)

- Microsoft

  v. Throughputer Inc (IPR2022-00757)

- Mom Enterprises

  v. Ddrops Company (Case No. 1:22-cv-00332)

- MLC Intellectual Property

v. MicronTech (Case No. 3:14-cv-03657-SI)

- Nearmap Inc

  v. EagleView Technologies (IPR2022-01009)

- Neuroderm Ltd.

  v. Abbvie, Inc (Case No. PGR2022-00040)

- Realtek Semiconductor

  v. Future Link (IPR2021-01182)

- Quectel

  v. Koninklijke Philips (Case No. 1:20-cv-01710)

- Samsung

  v. Aire Technology (IPR2022-00877)

  v. Bell Northern Research (Case No. 2:19-cv-00286-JRG)

  v. Communication Technologies Inc (IPR2022-01221)

  v. Jawbone Innovations (IPR2022-00865)

  v. MemoryWeb LLC (IPR2022-00885)

  v. Dodots Licensing Solutions (IPR2023-00701)

  v. Telefonaktiebolaget LM Ericsson (IPR2021-00615)

- Texas Instruments

  v. Vantage Micro LLC (IPR2020-01261)

- Xilinx

  v. Sentient Sensors LCC (Case No. 1:22-cv-00173)

Groombridge Wu

- Nearmap

  v. Eagle View Technologies Inc. and Pictometry International Corp. (Case No. 2:21-cv-00283-TS-DAO)

Irell & Manella

- Curium

O'Melveny & Myers

- Apple

  v. Maxell (Case No. 5:19-cv-00036-RWS)

- Disney Media & Entertainment Distribution LLC

  v. Digital Media Technology Holdings, LLC (Case No. 2:22-cv-01642)

- Micron Technology Inc.

  v. Besang Inc (IPR2023-00900)

- Samsung

  v. Daedalus Prime LLC (1335 Investigation)

Perkins-Coie

- Amazon

  v. Nokia (IPR2024-00847 and IPR2024-00848)

- Heru Industries
  - v. The UAB Research Foundation (IPR2022-01148)
- Intel Corporation
  - v. BeSang Inc. (IPR2023-00991)
  - v. BitMICRO (Case No. 5:23-cv-00625)
  - v. Telefonaktiebolaget L M Ericsson (IPR2024-00610)
- Realtek Semiconductor
  - v. Future Link (IPR2021-01182)
- Twitter Inc
  - v. VOIP-Pal.com (Case No. 3:20-cv-02397-JD)
- TCL Industries
  - v. Koninklijke Philips NV (IPR2021-00495, IPR2021-00496 and IPR2021-00497)

Pillsbury Winthrop Shaw Pittman

- Intel
  - v. FG SRC LLC (Case No. 6:20-cv-00315)
- Gravel Rating Systems
  - v. Costco (Case No. 4:21-cv-149)
  - v. Lowe's Home Centers (Case No. 4:21-cv-150)
  - v. T-Mobile USA (Case No. 4:21-cv-152)
  - v. Kohl's Inc. (Case No. 4:21-cv-258)
  - v. Under Armor (Case No. 4:21-cv-356)

Quinn Emanuel

- ServiceNow, Inc.

  v. InQuisient, Inc. (Case No. 22-900-CJB)

- Wolfspeed

  v. The Trustees of Purdue University (Case No. 1:2021-cv-00840)

Sheppard, Mullin, Richter & Hampton LLP

- Cadence Design Systems Inc.

  v. Semiconductor Design Technologies (Case No. 3:23-cv-01001)

Stern, Kessler, Goldstein & Fox

- Preliminary Research

Willkie, Farr & Gallagher LLP

- Neurent

  v. The Foundry, LLC (IPR2024-00669)

- Netflix, Inc.

  v. VideoLabs, Inc. (IPR2023-00628)

APPENDIX YE01

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003    OCoLC
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210 0  J. Electrochem. Soc.
222  0 Journal of the Electrochemical Society
245 00 Journal of the Electrochemical Society.
246 1  |iAt head of title, <2012-> :|aJES
260    New York, N.Y. :|bElectrochemical Society,|c1948-
300    volumes :|billustrations, portraits ;|c23-29 cm
310    Monthly
336    text|btxt|2rdacontent
337    unmediated|bn|2rdamedia
338    volume|bnc|2rdacarrier
362 0  Vol. 93, no. 1 (Jan. 1948)-
500    Title from cover.
500    Imprint varies.
500    Latest issue consulted: Vol. 159, no. 10 (2012).
510 1  Applied science & technology index|x0003-6986
510 2  Abstract bulletin of the Institute of Paper Chemistry
       |x0020-3033
510 2  Art and archaeology technical abstracts|x0004-2994
510 2  Chemical abstracts|x0009-2258
510 2  Coal abstracts|x0309-4979
510 2  Computer & control abstracts|x0036-8113|b1968-
510 2  Electrical & electronics abstracts|x0036-8105|b1968-
510 2  Energy research abstracts|x0160-3604
510 2  Engineering index annual (1968)|x0360-8557
510 2  International aerospace abstracts|x0020-5842
510 2  Life sciences collection
510 2  Metals abstracts|x0026-0924
510 2  MINPROC
510 2  Physics abstracts. Science abstracts. Series A|x0036-8091
       |b1968-
510 0  Selected water resources abstracts|x0037-136X
555    Vols. 93 (1948)-98 (1951), (Includes index to its
       Transactions. v. 81 (1942)-92 (1947),  1 v.; Vols. 99
       (1952)-108 (1961),  1 v.; Vols. 109 (1962)-118 (1971).  1
       v.
580    Formed by the union of: Bulletin of the Electrochemical
       Society, and: Preprint - Electrochemical Society and
       continues the vol. numbering of the latter.
580    Absorbed in 1950: Transactions of the Electrochemical
       Society.
650  0 Electrochemistry|vPeriodicals.
650  0 Electrochemistry|xSocieties, etc.
710 2  Electrochemical Society.
780 14 |tBulletin of the Electrochemical Society|x0898-1388
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        |aOU|aViBlbV
935     ADM-3769
997     xagb
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Location	Carnegie Library of Pittsburgh - Off Site Storage (Please ask for assistance)
Lib Has	Volume 97 (1950) to Volume 116 (1969)., (Shelved as: Electrochemical Society Journal)
Identity	Reference Services
Location	CLP Main (Oakland) Second Floor - Magazines
Lib Has	Volume 117 (1970) to Volume 159 (2012)., (Shelved as: Electrochemical Society Journal)

eiNetwork
New Library Catalog Suggest a Purchase Questions Site Requirement
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Title	**Journal of the Electrochemical Society.**
Publisher	New York, N.Y. : Electrochemical Society, 1948-
Description	volumes : illustrations, portraits ; 23-29 cm
Frequency	Monthly
Pub Date	Vol. 93, no. 1 (Jan. 1948)-

Location	Carnegie Library of Pittsburgh - Off Site Storage (Please ask for assistance)
Lib Has	Volume 97 (1950) to Volume 116 (1969)., (Shelved as: Electrochemical Society Journal)
Identity	Reference Services
Location	CLP Main (Oakland) Second Floor - Magazines
Lib Has	Volume 117 (1970) to Volume 159 (2012)., (Shelved as: Electrochemical Society Journal)

Details

Note	Title from cover. Imprint varies. Latest issue consulted: Vol. 159, no. 10 (2012).
Indexed In:	Applied science & technology index 0003-6986 Abstract bulletin of the Institute of Paper Chemistry 0020-3033 Art and archaeology technical abstracts 0004-2994 Chemical abstracts 0009-2258 Coal abstracts 0309-4979 Computer & control abstracts 0036-8113 1968- Electrical & electronics abstracts 0036-8105 1968- Energy research abstracts 0160-3604 Engineering index annual (1968) 0360-8557 International aerospace abstracts 0020-5842 Life sciences collection Metals abstracts 0026-0924 MINPROC Physics abstracts. Science abstracts. Series A 0036-8091 1968- Selected water resources abstracts 0037-136X
Indexes	Vols. 93 (1948)-98 (1951), (Includes index to its Transactions. v. 81 (1942)-92 (1947), 1 v.; Vols. 99 (1952)-108 (1961), 1 v.; Vols. 109 (1962)-118 (1971). 1 v.
Note	Formed by the union of: Bulletin of the Electrochemical Society, and: Preprint - Electrochemical Society and continues the vol. numbering of the latter. Absorbed in 1950: Transactions of the Electrochemical Society.
Subject	Electrochemistry -- Periodicals. Electrochemistry -- Societies, etc.
Addt'l Author	Electrochemical Society.
Key Title	J. Electrochem. Soc. Journal of the Electrochemical Society
Other Title	At head of title, <2012-> : JES
Formed By	Bulletin of the Electrochemical Society

Show similar items

	Electrochemical Society. Preprint - Electrochemical Society
	Show similar items
Absorbed	Transactions of the Electrochemical Society 1950
	Show similar items
Cont In Part	Electrochemical Society interface
	Show similar items
ISSN	**0013-4651**

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APPENDIX YE02


ELECTROCHEMICAL
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139
APR-JUNE
1992

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June 1992

Vol. 139 • No. 6

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(USPS 284-140)
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ELECTROCHEMICAL SOCIETY LETTERS

Brittle Fracture of Cu-30 Au Induced by a Surface Layer
J. S. Chen, M. Salmeron, T. M. Devine L55

First Observation of Electrochemiluminescence in Molten Salt Solutions
G. Mamantov, K. D. Sienerth, C. W. Lee, J. E. Coffield, S. D. Williams L58

Patterned Deposition of Copper on Poly(tetrafluoroethylene)
R. R. Rye, K. M. Chi, M. Hampden-Smith, T. T. Kodas L60

Laser-Enhanced Electrodeposition of Lead-Tin Solder
Q. Lin, K. G. Sheppard, M. Datta, L. T. Romankiw L62

TECHNICAL PAPERS

ELECTROCHEMICAL SCIENCE AND TECHNOLOGY

Electrochemical Properties of Aluminum in Weakly Acidic Sodium Chloride Solutions. II. Influence of the Electrolyte Additives
J. F. Equey, S. Muller, J. Desilvestro, O. Haas 1499

The Influence of Active Site Loading, Electrolyte Composition, and Temperature on Charge Transfer Reactions of Poly(N-vinylimidazole) Films Containing Pendant $[Os(bipy)2C1]^+$ Moieties
R. J. Forster, J. G. Vos 1503

The Rechargeable $Li_xTiS_2/LiAlCl_4/Li_{1-x}CoO_2$ Solid-State Cell
E. J. Plichta, W. K. Behl, D. Vujic, W. H. S. Chang, D. M. Schleich 1509

Kinetics of Intercalation of Lithium into $NbSe_3$ and TiS_2 Cathodes
B. V. Ratnakumar, G. Nagasubramanian, S. Di Stefano, C. P. Bankston 1513

Preparation and Characterization of Modified Electrode by Self-Assembling Ferrocene Derivative
H. Tsutsumi, S. Furumoto, M. Morita, Y. Matsuda 1522

***In Situ* Raman Spectra of Pyridine and Pyridinium Chloride Adsorbed on Iron in K_2SO_4 and H_2SO_4 Solutions**
K. Aramaki, M. Ohi, J. Uehara 1525

Corrosion and Passivation of Fe and FeN Films
V. Brusic, G. S. Frankel, B. M. Rush, A. G. Schrott, C. Jahnes, M. A. Russak, T. Petersen 1530

Reactive Deposition of Cobalt Electrodes. VIII. Effect of Oxygen Reduction on the Deposition of Cobalt in Co(II) Chloride DMF Solution
C. Q. Cui, S. P. Jiang, A. C. Tseung 1535

The Electrical Conductivity of Solid/Liquid Coexisting Systems: Composition Dependence of the Electrical Conductivity
S. Deki, M. Mizuhata, K. Nakamura, A. Kajinami, Y. Kanaji 1544

The Effects of Nickel Oxide Cathode Dissolution on Molten Carbonate Fuel Cell Life
H. R. Kunz, J. W. Pandolfo 1549

Comparing Electrochemical Impedance Spectroscopy Methods for Estimating the Degree of Delamination of Organic Coatings on Steel
S. A. McCluney, S. N. Popova, B. N. Popov, R. E. White, R. B. Griffin 1556

Corrosion Mechanism of Sputter-Deposited TbFe Thin Films in Aqueous Environment
N. Akao, K. Sugimoto 1560

Grazing Incidence X-Ray and Electrochemical Study of Thin Film Copper(111) on Mica
G. L. Borges, M. G. Samant, K. Ashley 1565

Chaos during the Growth of an Artificial Pit
.....S. G. Corcoran, K. W. Sieradzki 1568

Surface Analysis of Corrosion Pits Initiated at MnS Inclusions in 304 Stainless Steel
.....R. Ke, R. C. Alkire 1573

High Field Pulse Plating: Gold on Platinum Electrodes
.....C. C. Segal, A. B. Chase, A. M. Young 1580

On the Passive Films and Anodic Behavior of Samarium in Various Aqueous Solutions
.....H. H. Yang, N. Hara, K. Sugimoto 1586

Role of Overpotential on Texture, Morphology, and Ductility of Electrodeposited Copper Foils for Printed Circuit Board Applications
.....X. Ye, M. De Bonte, J. P. Celis, J. R. Roos 1592

Generation of Hydrous Oxide Species at Carbon-Supported, Finely Divided Platinum Surfaces
.....L. D. Burke, J. F. Rohan 1600

Electrochemical Reduction of Carbon Dioxide in Water: Analysis of Reaction Mechanism on Ruthenium-Titanium-Oxide
.....A. Bandi, H.-M. Kühne 1605

Unusual, Non-Cottrell Behavior of Ionic Transport in Thin Cells and in Films
.....R. P. Buck, T. M. Nahir, R. Mackel, H.-D. Liess 1611

Comparison of the Quartz-Crystal Microbalance and the Double-Layer Capacitance Methods for Measuring the Kinetics of the Adsorption of Bovine Serum Albumin onto a Gold Electrode
.....F. Lacour, R. Torresi, C. Gabrielli, A. Caprani 1619

AC Impedance Study of Anodically Formed Salt Films on Iron in Chloride Solution
.....R. D. Grimm, A. C. West, D. Landolt 1622

Photoelectrochemistry of Semiconductor ZnO Particulate Films
.....S. Hotchandani, P. V. Kamat 1630

The Platinum Microelectrode/Nafion Interface: An Electrochemical Impedance Spectroscopic Analysis of Oxygen Reduction Kinetics and Nafion Characteristics
.....A. Parthasarathy, B. B. Dave, S. Srinivasan, A. J. Appleby, C. R. Martin 1634

Solution of Laplace's Equation to Calculate the Ohmic Potential Drop for Hexagonally Shaped Scratches
.....J. Rojo, C. Thompson, A. Bronson 1641

Poly(ethylene oxide)-Based Zn(II) Halide Electrolytes
.....H. Yang, G. C. Farrington 1646

SOLID-STATE SCIENCE AND TECHNOLOGY

Compositional and Microstructural Characterization of RuO_2-TiO_2 Catalysts Synthesized by the Sol-Gel Method
.....M. Guglielmi, P. Colombo, G. Battaglin, A. Bosco-Boscoletto, A. De Battisti, V. Rigato 1655

The Preparation of Superconducting $YBa_2Cu_3O_{7-y}$/Ag Microlaminates by an Oscillating Oxidation Scheme
.....K. H. Sandhage 1661

Ionic Conductivity and Phase Transformation in Gd_2O_3-Stabilized Bi_2O_3
.....P. Su, A. V. Virkar 1671

Deep Ultraviolet Lithography of Monolayer Films with Selective Electroless Metallization
.....J. M. Calvert, M. S. Chen, C. S. Dulcey, J. H. Georger, M. C. Peckerar, J. M. Schnur, P. E. Schoen 1677

The Effects of Preheatings on Axial Oxygen Precipitation Uniformity in Czochralski Silicon Crystals
.....H. D. Chiou 1680

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m^{-3} NaCl (pH 6.5) and 0.005 kmol · m^{-3} Na_2SO_4 (pH 6.5), however, Sm dissolves actively from the corrosion potential and does not passivate.

2. The thickness of passive films formed on Sm in solutions of phosphate (pH 2.98 and 6.86), borate (pH 8.45), and 0.1 kmol · m^{-3} NaOH (pH 13.1) increased with increasing potential. At a given potential, the thickness of the films was in the following order:

NaOH (pH 13.1) < phosphate (pH 6.86) < borate (pH 8.45) < phosphate (pH 2.98)

In any solution, the thickness of transpassive films increased sharply with increasing potential.

3. The optical constants, $N_2 = n_2 - ik_2$, of passive films measured at 546.1 nm were dependent on the composition and pH of solution. The value of n_2 for the films in the solutions examined increased in the following order:

phosphate (pH 2.98) < borate (pH 8.45) < phosphate (pH 6.86) < NaOH (pH 13.1)

The value of $n_2 = 2.00$ for the film in NaOH solution (pH 13.1) is close to the refractive index of Sm_2O_3. The values of n_2 for transpassive films were smaller than those for passive films and approximately independent of composition and pH of the solutions.

4. The passive film formed in an acidic phosphate solution (pH 2.98) is mainly composed of hydrous Sm(III) phosphate ($SmPO_4 \cdot xH_2O$), and that formed in a neutral phosphate solution (pH 6.86) contains both $SmPO_4 \cdot xH_2O$ and Sm(III) oxide. The passive films formed in neutral borate (pH 8.45) and alkaline NaOH (pH 13.1) solutions consist essentially of Sm(III) oxide and hydroxide. The transpassive film formed in the neutral phosphate solution (pH 6.86) is composed of $SmPO_4 \cdot xH_2O$ and Sm(III) hydroxide, and that in the alkaline NaOH solution (pH 13.1) of Sm(III) oxide and hydroxide.

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Role of Overpotential on Texture, Morphology and Ductility of Electrodeposited Copper Foils for Printed Circuit Board Applications

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ABSTRACT

A study was made to correlate different electrodeposition parameters, like, *e.g.*, cathodic overpotential, bath composition, and bath ageing, with characteristics as crystallographic texture and roughness, and the ductility of electrolytic copper foils. Copper foils with a low (220) preferred crystallographic orientation, and a smooth surface are obtained when depositing at 87 to 113 mV cathodic overpotential from copper sulfate solutions with a low chloride content. Under these plating conditions copper foils with the highest ductility were achieved.

In comparison with cast and wrought materials, electrodeposited materials often suffer from a low ductility. So, as for example, cracks in printed circuit boards (PCB) are commonly attributed to the low ductility of copper deposited in the plated through holes (PTH) that act as connectors between copper layers within the PCB. As a consequence the electrodeposited copper cannot accommodate the deformation during soldering caused by the differential thermal expansion between the substrate of a printed circuit board and the electrodeposited copper (1, 2). Although, the ductility of the electrodeposited copper has been intensively studied (3-6), the relationship between

ductility of electrodeposited copper, structural characteristics of the electrodeposits, and electrodeposition parameters is still unclear.

The majority of investigations on the ductility of copper layers in PCB have been carried out under a uniaxial stress state. However, the ductility of a metal varies with the stress state under which the material is tested (7, 8). The stress state of electrodeposited copper in the plated through holes of the PCB is definitely a biaxial stress state (9). Therefore the ductility of such layers has to be assessed under biaxial stress state conditions.

Related to ductility, Marciniak and Kuczynski (10) stated that the deformation behavior of metallic sheets under a biaxial stress state is influenced by the initial topographical irregularity, the ratio of width strain to thickness strain in an uniaxial tensile test, the strain hardening exponent, and the initial strain. Barlat and co-workers (11-13) suggested that the limiting strain of sheet materials was influenced by the yield surface shape. This yield surface shape can be computed from orientation distribution function (ODF) measurements. The yield surface shape then is characterized by the ratio, ρ^*, of the plane strain flow stress to the balanced biaxial flow stress. The larger the ratio ρ^* is, the larger the limiting strain.

Related to structural characteristics, the crystallographic texture and the morphology of copper electrocoatings depend on the electrodeposition parameters such as plating bath composition, pH, overpotential, current density, substrate, etc. (14). Among them the cathodic overpotential seems to be the most important controlling parameter (15).

In the present work, the effect of the cathodic overpotential on the ductility is presented as well as the effect of the crystallographic texture and the roughness on the ductility of copper foils. The ductility of copper foils was investigated under a biaxial stress state by means of a mechanical stretching test.

Experimental

The plating bath was prepared from analytical grade chemicals and contained 0.36*M* $CuSO_4 \cdot 5H_2O$ and 2.04*M* H_2SO_4. Sodium chloride was used as an additive. Electrodeposition of copper was carried out in a 1.5 liter jacketed cell. During deposition the temperature was controlled to within ± 0.5°C. The rotating disk cathode was made of stainless steel (ϕ 52 mm) sheathed by a Teflon cylinder with an outer diameter of 70 mm. The rotation speed was controlled at 300 rpm. The anode was a copper disk of electrolytically deposited copper (ϕ 80 mm). This anode was located at the bottom of the cell. A polypropylene bag was used to cover the anode. The distance between cathode and anode was 10 cm. A PAR potentiostat (Model 173 with plug in Model 179) was used for electrodepositing copper layers. A saturated mercury sulfate electrode (SSE) was used as a reference electrode.

In order to study the effect of ageing of the electrolytes on the ductility, solutions were left unstirred for either 3 or 16 h before the next electrodeposition was carried out. Copper foils deposited after a long settling time of 16 h are labelled L; the foils deposited within three hours after production of the previous deposit are labelled S.

In some cases an activated carbon pretreatment was carried out in a beaker of 1 liter by adding 2 g/liter activated carbon to the stock solution stirred at 80°C for 2 h. Finally a filtration through a 0.22 μm filter paper was done. It was found that after purification the concentration of Cl^- increased from 0 to 5 ppm brought in by activated carbon containing chloride (9). The determination of the chloride is based on a potentiometric method using 0.1655*M* silver nitrate solution as reagent.

Before electrodeposition, the stainless steel cathode was first cathodically cleaned for 10-20 s at a current density of 25-50 A/dm² in a solution containing 2.04 *M* H_2SO_4 at room temperature. After cleaning, the cathode was washed with tap water followed by rinsing with distilled water, and passivated in a 40% HNO_3 solution for 8 h. After passivation, the cathode was rinsed first with tap water for 15 min and finally with distilled water. In this way the copper deposits could be easily peeled off from the stainless steel cathode.

The thickness of the electrodeposited foils was about 20 μm. The thickness was measured with a Fisher Multiscope. Roughness average (R_a) was measured with a Form Talysurf. A roughness factor α, defined as the ratio of the roughness average over the foil thickness, was calculated for each specimen.

Texture was determined by x-ray diffraction (Philips PW 1010 30). The x-ray source was a Cu-K_α radiation. The crystallographic texture is presented as a normalized peak intensity (NPI) defined as

$$NPI_{(hkl)} = P_{(hkl)}/P^*_{(hkl)} \times 1/\Sigma[P_{(hkl)}/P^*_{(hkl)}] \quad [1]$$

with $P_{(hkl)}$ the relative (hkl)peak intensity for a given coating, and $P^*_{(hkl)}$ the relative (hkl)peak intensity for a randomly oriented copper powder sample with a thickness of 25 μm. For selected specimens the texture was measured with a goniometer (Siemens). The diffraction of the (111), (200), (220), and (311), planes were measured to determine the pole figures. The orientation distribution functions (ODF) were then calculated based on the pole figure data. The yield loci of (111)[110] slip systems were calculated by using the Orientation Distribution Functions [16]. The Orientation Distribution Functions, the inverse pole figures and the yield locus were computed with a "MTM-QTA Version 2" software system written by Van Houtte and distributed by Siemens. On the yield locus, the plane strain flow stress (σ_p) and the balanced biaxial flow stress (σ_b) can be distinguished according to Barlat (11). Then the stress ratio (ρ^*) is obtained as σ_p/σ_b.

The microstructure was observed in a transmission electron microscope (TEM), JEM-200CX. Specimens were prepared by jet electropolishing. The polishing solution was composed of 33 weight percent (w/o) HNO_3 and 67 w/o methanol. Electropolishing was carried out at −35°C and 8 V. The average grain size was determined based on five to ten pictures of each specimen (a total of about one hundred grains) taken randomly with the TEM. When the determination of the boundary between individual grains was difficult in a bright field image, diffraction patterns and dark field imaging were used to distinguish the real boundaries.

To measure polarization curves, a rotating disk electrode of ϕ 52 mm containing a platinum electrode of ϕ 3 mm located at the center of the disk was used. Galvanostatic polarization curves were stepwise deduced from potential measurements at eight current densities in the range of 0.4 to 3.2 A/dm².

The ductility of copper foils was tested by means of a mechanical stretching tester (9). A scheme of the stretching tester is shown in Fig. 1. On each foil, triplicate tests were done. Testing sectors were clamped in a die of inner working diameter ϕ 5 mm. The stretching test area was selected at 15 mm distance from the center of the electrodeposited copper disks. While testing, the load and the displacement of the punch head were recorded. The distance from the point at which the load starts rising to the point at which the specimen ruptures is defined as the penetration depth, and is used as a criterion for the ductility under biaxial stress state. From a large number of introductory

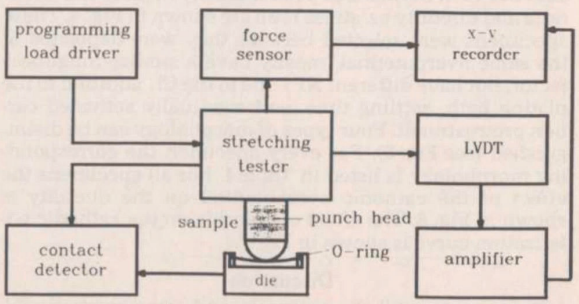


Fig. 1. Scheme of stretching tester.

Table I. Electrodeposition conditions, ductility, roughness, thickness, and morphology type for specimens tested.

No.	η (mV)	Current density (A/dm²)	Cl^- (ppm)	Pretreatment	Morphology	t	Penetration depth (mm)	h_0 (μm)	R_a (μm)	α
1	87	0.47	5	yes	b	S	1.07	19.7	0.36	0.019
2	87	0.44	5	yes	b	L	0.96	19.4	0.60	0.031
3	87	0.44	5	yes	b	S	0.99	18.5	0.50	0.027
4	87	0.45	5	yes	b	S	1.02	19.7	0.63	0.032
5	87	0.47	5	yes	b	S	1.04	20.9	0.55	0.026
6	87	0.47	25	yes	b	S	0.97	20.4	0.51	0.025
7	113	0.80	5	yes	d	L	0.87	17.7	0.75	0.042
8	113	0.66	5	yes	b	L	1.02	20.3	0.48	0.022
9	113	0.60	5	yes	b	S	1.03	20.4	0.68	0.033
10	113	0.60	5	yes	b	L	1.01	20.6	0.65	0.032
11	113	0.66	5	yes	b	S	1.01	20.1	0.79	0.039
12	113	1.10	5	yes	b	S	0.93	20.4	0.70	0.034
13	113	0.90	5	yes	b	L	0.82	22.3	1.85	0.083
14	113	0.70	10	yes	b	L	0.95	19.8	0.84	0.042
15	113	0.80	15	yes	b	L	0.93	20.5	0.68	0.033
16	113	0.90	0	no	b	S	0.92	20.1	0.81	0.040
17	113	0.70	5	no	b	S	1.06	21.1	0.58	0.027
18	113	0.90	10	no	b	S	1.09	21.0	0.38	0.018
19	120	1.10	0	no	b	L	0.97	21.4	0.60	0.028
20	120	1.10	0	no	b	S	0.93	21.7	0.59	0.027
21	120	0.70	5	no	b	S	1.06	19.9	0.42	0.021
22	120	0.70	10	no	b	L	1.02	20.9	0.38	0.018
23	120	0.85	20	no	b	S	0.90	19.4	0.37	0.019
24	120	0.81	20	no	b	S	0.93	19.7	0.60	0.031
25	158	1.00	5	yes	b	S	1.00	20.5	0.57	0.028
26	158	1.46	5	yes	d	L	0.81	21.3	1.73	0.081
27	158	1.18	5	yes	b	S	0.95	20.1	0.36	0.018
28	158	0.90	5	yes	b	L	0.95	21.9	1.31	0.060
29	200	1.27	5	yes	b	S	0.97	19.8	0.42	0.021
30	200	1.93	5	yes	b	L	0.96	20.1	0.87	0.043
31	200	1.70	20	no	a	S	0.90	21.8	0.48	0.022
32	250	3.30	0	no	c	L	0.84	20.7	0.62	0.030
33	250	3.20	0	no	c	L	0.83	19.1	0.36	0.019
34	250	3.20	0	no	c	S	0.72	20.8	0.91	0.044
35	250	2.90	5	no	a	S	0.63	19.0	0.41	0.021
36	250	3.10	10	no	a	S	0.61	19.8	0.58	0.029
37	250	3.30	20	no	a	L	0.76	19.8	0.48	0.024
38	250	3.20	20	no	a	L	0.72	21.1	0.78	0.037
39	250	2.90	20	no	a	S	0.60	20.2	0.38	0.019
40	250	3.30	40	no	a	S	0.53	19.7	0.39	0.020
41	250	3.30	5	yes	c	S	0.74	21.5	1.16	0.054
42	250	3.10	10	yes	a	S	0.70	21.0	0.93	0.044
43	250	3.10	15	yes	a	S	0.70	22.1	1.43	0.065
44	250	3.00	25	yes	a	L	0.53	19.2	0.42	0.022

Note: η, overpotential, *t*, ageing time of solution, (L for a long time and S for a short time); h_0, thickness; R_a, average roughness; α, roughness factor.

tests, it appeared that the reproducibility obtained in this equipment is very high as compared to other mechanical bulge tests. The standard deviation is less than 4 % (9).

Results

The electrodeposition conditions and results for penetration depth, thickness, roughness, and corresponding roughness factor are listed in Table I. The peak intensities of the (111), (200), and (220) diffraction lines and the corresponding NPI of specimens and powder sample are listed in Table II. A typical inverse pole figure, two typical yield loci, and the corresponding stress ratio ρ* are shown in Fig. 2. For five specimens their ρ* values are listed in Table II. The NPI of all specimens is shown in Fig. 3. The center point of this triangle corresponds to the state of random orientation. The three corners represent a 100% orientation of (111), (100), or (110), respectively. The relationship between normalized peak intensity of (220) and stress ratio and ductility *vs.* stress ratio are shown in Fig. 4. These specimens were selected because they were deposited at the same overpotential, mostly have a similar roughness factor, but have different NPI due to the Cl^- addition to the plating bath, settling time, and eventually activated carbon pretreatment. Four types of morphology can be distinguished (see Fig. 5). For every specimen the corresponding morphology is listed in Table I. For all specimens the effect of the cathodic overpotential on the ductility is shown in Fig. 6. The effect of chloride on the cathodic polarization curve is shown in Fig. 7.

Discussion

Texture of copper electrodeposited from acid copper sulfate solutions.—From a typical inverse pole figure (Fig. 2a) it can be deduced that the texture of the specimen is a fiber texture. The direction of the fiber axis is normal to the surface of the copper coating, in other words, parallel to the direction of the electric field during deposition. According to the measured textures (Fig. 3), the majority of specimens have more or less a (220) fiber texture. Notwithstanding the fact that the crystallographic texture of metal deposits depends on the processing parameters, such as bath composition, pH, overpotential, deposition rate (current density), substrate, mass-transport condition, etc., information which is not always available in earlier published work, some comparison with the present research is possible. O'Keefe and Hurst (17) found that without additives the (220) orientation was predominant. With addition of chloride ions, (220) was the predominant orientation, but at increasing chloride ion concentration, the occurrence of the (111) orientation also increases. Lakshmanan *et al.* (18) revealed that copper deposited from acid copper sulfate solutions with a chloride ion concentration up to 10 ppm yields (220) oriented deposits. At higher Cl^- concentration, the (111) orientation appears preferentially. Recently, Fukunaka *et al.* (19) published texture data for copper deposited from a stagnant acid copper sulfate solution containing 0.6*M* $CuSO_4$ and 1.85*M* H_2SO_4. According to their data, the (220) texture was the main texture up to a cathodic overpotential of 150 mV. The presence of a predominant (220) orientation in copper deposits is consistent with this study. However, that a (111) texture develops at increasing chloride content as observed by Lakshmanan and O'Keefe is not in agreement with this study (see further the section on Effect of bath composition and ageing). This could be due to the constant current density they used instead of the constant overpotential used in this study.

Table II. Relative peak intensity, corresponding NPI and stress ratio (ρ^*) for specimens tested.

No.	(111)	(200)	(220)	(111)	(200)	(220)	ρ^*
	Measured			Normalized			
Random	100.0	49.5	12.0	33.3	33.3	33.3	
1	100.0	44.4	86.7	11.0	9.8	79.2	
2	100.0	31.6	16.5	33.2	21.2	45.5	
3	100.0	45.5	69.7	12.9	11.9	75.2	
4	100.0	28.8	16.4	33.9	19.7	46.4	
5	100.0	35.9	53.8	16.1	11.7	72.2	
6	100.0	34.0	28.3	24.7	17.0	58.3	
7	100.0	33.7	15.4	33.8	23.0	43.3	
8	100.0	23.6	27.0	26.9	12.8	60.3	
9	100.0	31.0	71.4	13.2	8.3	78.6	
10	100.0	22.2	22.2	30.3	13.6	56.1	
11	100.0	29.4	88.2	11.2	6.6	82.2	
12	100.0	24.1	53.4	16.8	8.2	75.0	
13	100.0	33.3	18.5	31.1	20.9	48.0	
14	100.0	46.3	10.4	35.7	33.4	30.9	
15	100.0	52.6	21.1	26.2	27.9	46.0	
16	100.0	25.5	30.0	24.9	12.8	62.3	
17	100.0	41.0	43.6	18.3	15.2	66.5	
18	98.1	50.0	100.0	9.5	9.8	80.7	
19	100.0	29.2	18.5	32.0	18.9	49.2	
20	100.0	31.3	31.3	23.6	14.9	61.5	
21	81.5	48.1	100.0	8.1	9.6	82.3	
22	100.0	32.7	34.6	22.0	14.5	63.5	
23	67.5	32.5	100.0	7.0	6.8	86.2	
24	70.6	41.2	100.0	7.2	8.4	84.4	
25	100.0	40.5	94.6	10.3	8.4	81.3	
26	100.0	13.8	13.8	41.1	11.5	47.4	
27	100.0	28.9	75.6	12.7	7.4	79.9	
28	100.0	26.6	18.1	32.8	17.6	49.5	
29	100.0	27.5	75.0	12.8	7.1	80.1	
30	100.0	26.4	18.4	32.6	17.4	50.0	
31	84.6	34.6	100.0	8.6	7.1	84.4	
32	100.0	30.0	15.0	35.0	21.2	43.8	
33	100.0	25.5	12.7	38.8	20.0	41.2	
34	100.0	24.6	11.4	40.9	20.3	38.8	
35	9.4	4.7	100.0	1.1	1.1	97.8	1.047
36	29.2	8.3	100.0	3.3	1.9	94.8	1.053
37	100.0	25.7	42.9	19.6	10.2	70.2	
38	100.0	25.0	83.3	11.8	6.0	82.2	1.072
39	16.4	5.5	100.0	1.9	1.3	96.8	
40	4.1	2.1	100.0	0.5	0.5	99.0	1.033
41	100.0	21.7	10.0	44.0	19.3	36.7	1.089
42	100.0	28.7	20.4	30.5	17.7	51.8	
43	100.0	32.6	16.3	33.2	21.8	45.0	
44	5.5	2.7	100.0	0.6	0.7	98.7	

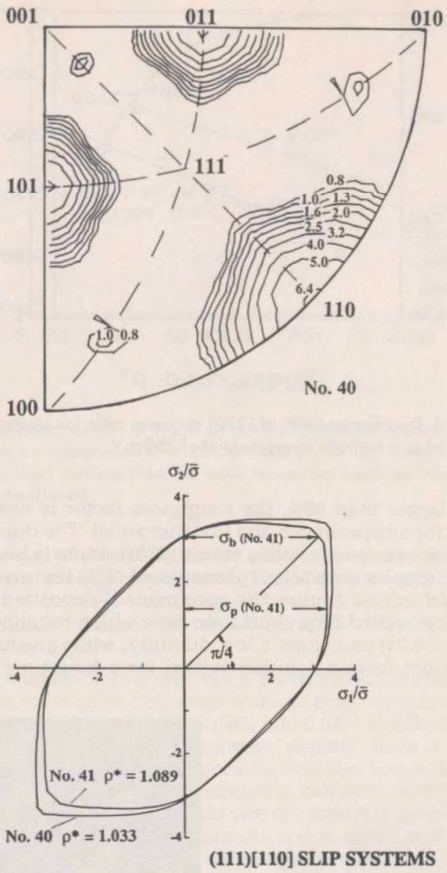


Fig. 2. Inverse pole figure (a, top) of specimen No. 40 and yield loci (b, bottom) of specimens No. 40 and 41.

It is interesting to note that after normalizing the original data obtained by Lakshmanan and O'Keefe (see Fig. 8), no specimen appears with a (111) orientation. So, the (111) orientation is not increasing with chloride ion concentration as they mentioned, but in fact the (220) orientation component was less developed with increasing chloride. After normalization, the results obtained by Lakshmanan and O'Keefe seem to be in agreement with ours. For comparison of textures, the use of normalized texture data should thus be preferred to avoid incorrect conclusions to be drawn.

Texture and ductility.—It is well known that the texture of metallic sheets affects their deformation behavior. Sard and Weil (6) reported that the elongation of electrodeposited copper films with a <100> direction along the tensile axis was of 3.9 to 6.1%, while samples with a <110> direction along the tensile axis had an elongation of 13 to 25.8%.

The relationship between ductility and stress ratio ρ^* for copper foils produced at a cathodic overpotential of 250 mV is shown in Fig. 4. The ductility increase with increasing stress ratio confirms Barlat's hypothesis (11-13), and is consistent with the results of Van Vooren (20) who reported that with increasing ρ^*, Pd-Ni deposits with a higher ductility were obtained. As shown in Fig. 4, a relationship between ρ^* and the NPI of (220) also exists. The ρ^* of specimens can thus be estimated from the NPI without measuring a complete set of ODF. From Fig. 4, it can be seen that at high NPI of (220) the stress ratio ρ^* decreases very quickly, while the ductility is very sensitive to a change in texture (NPI) at higher (220) NPI. The relationship between ductility and the NPI of (220) is shown in Fig. 9 for all specimens with a roughness factor α <0.04. Although the data are widely scattered, it remains clear that the ductility decreases at very high NPI of (220). This tendency appears independently of the ageing time considered.

Roughness and ductility.—According to Marciniak and Kuczynski (10), a higher initial topographical irregularity leads to a lower ductility. In order to describe the surface irregularity, they used a model consisting of a groove in a foil, and defined the ratio of the depth of the groove to the thickness of specimen as the initial irregularity. As an approximation, the roughness factor (α) is used in this study to describe that surface irregularity.

The roughness factor α is indicated in Fig. 10 at each measuring point corresponding to specimens deposited at an overpotential of 250 mV. The settling time of the plating bath before electrodeposition is also indicated. At a NPI of

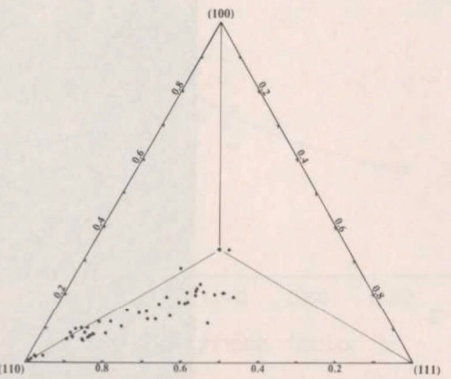


Fig. 3. Normalized x-ray peak intensity of all the electrodeposited copper foils tested (*: random orientation of copper powder sample).

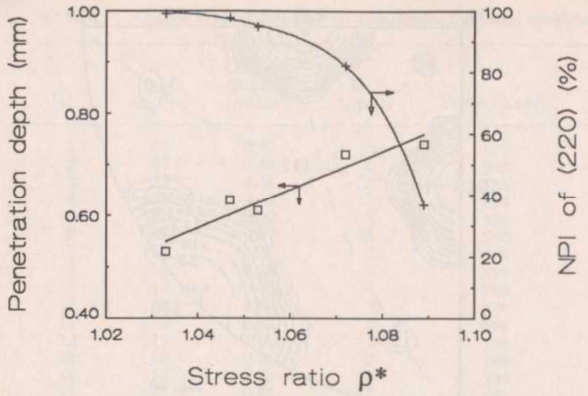


Fig. 4. Ductility and NPI of (220) *vs.* stress ratio for electrodeposits produced at a cathodic overpotential of 250 mV.

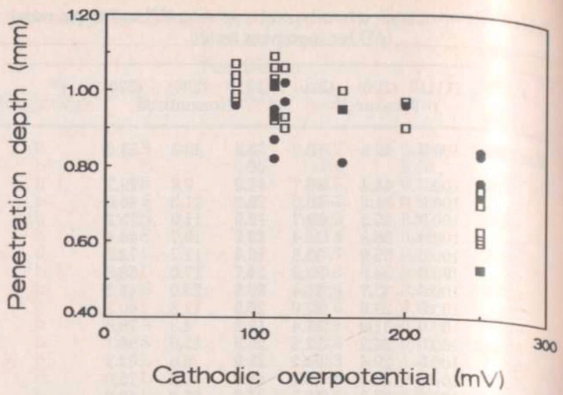


Fig. 6. Effect of overpotential on ductility for all copper foils tested. (●) Long settling time; (□) short settling time.

(220) larger than 90%, the roughness factor is nearly the same for all specimens and is rather small. The ductility of all these specimens with a strong (220) texture is low. However, samples with a less pronounced (220) texture can be divided in two groups: the specimens S deposited from a solution settled for a short time have a high roughness factor ($\alpha \geq 0.04$) and show a low ductility, while specimens L deposited from a solution settled for a long time have a lower roughness factor ($\alpha < 0.04$) and a higher ductility. The high surface roughness can be related to the cauliflower-type of morphology (see Fig. 5c).

The influence of the roughness factor on the ductility is also evident for specimens deposited at an overpotential of 113 mV, as is shown in Fig. 11. The NPI of (220) in this group is situated between 30.9% and 82.2% NPI of (220). It appears that at this overpotential the influence of the NPI

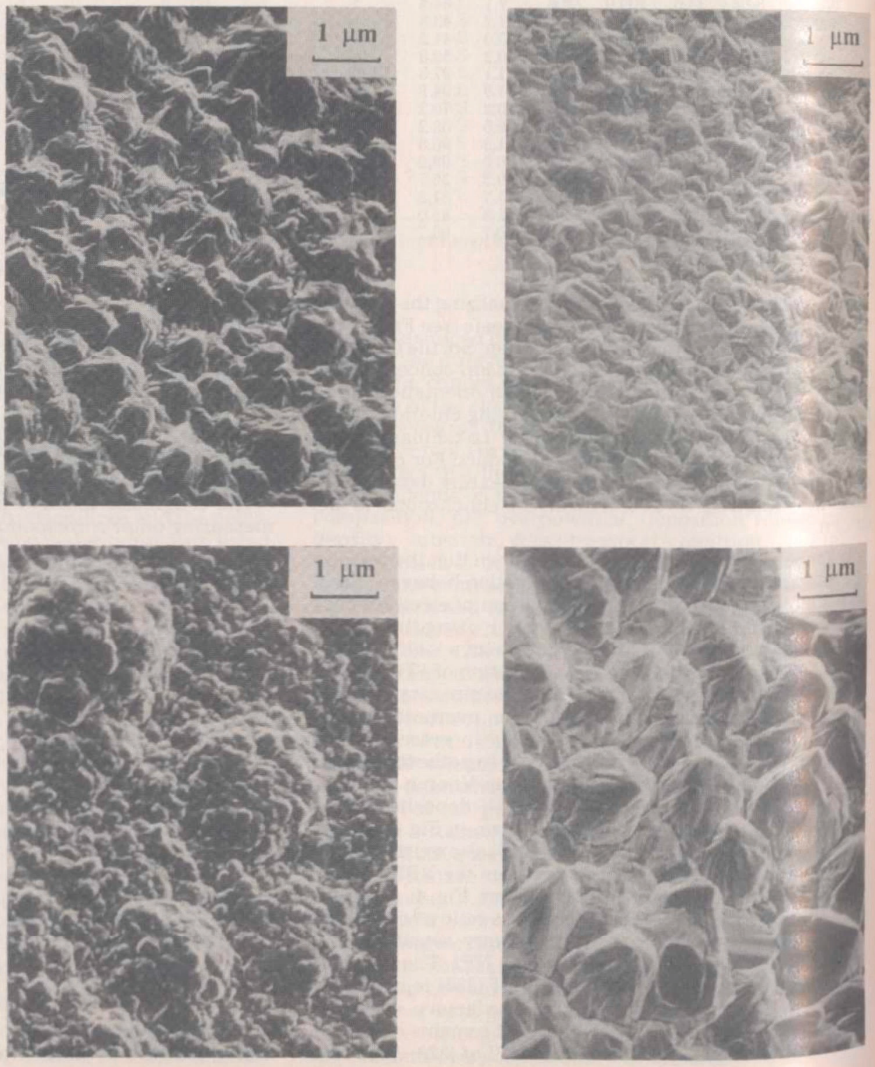


Fig. 5. Different morphologies obtained by electrodepositing at different process parameters as presented in Table I. (a, top left; b, top right; c, bottom left; d, bottom right)

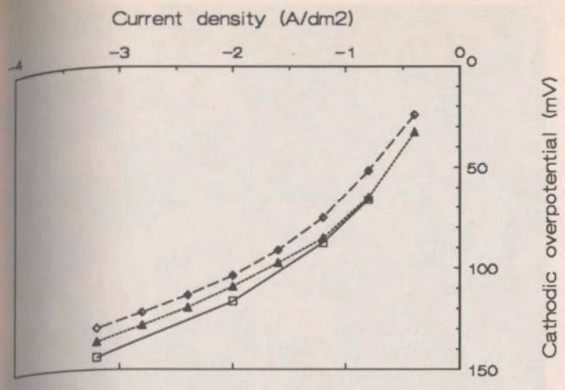


Fig. 7. Galvanostatic polarization curves recorded at 25°C in acid copper sulfate solutions containing 0.36M $CuSO_4 \cdot H_2O$, 2.04M H_2SO_4 and different chloride concentrations: (□) 0 ppm Cl^-; (▲) 20 ppm Cl^-; (◇) 80 ppm Cl^-.

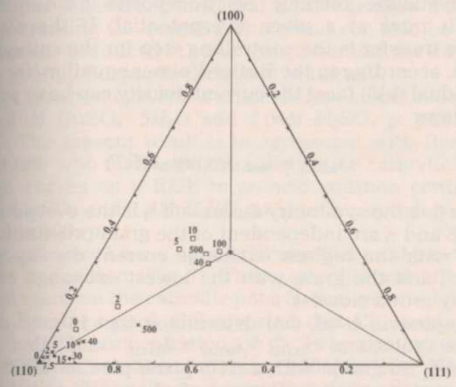


Fig. 8. Data of O'Keefe *et al.* (17) and Lakshmanan *et al.* (18) represented in a NPI triangle. (●) 3.98 A/dm² (17), (□) 1.5 A/dm² (18) (×) 3 A/dm² (18). Note: the numbers in the figure indicate the chloride concentration in ppm.

of (220) on the ductility is less pronounced, but that the influence of the roughness factor becomes important.

Cathodic overpotential and ductility.—In Fig. 6 the ductility of all 44 specimens mentioned in Table I is plotted as a function of the overpotential. It can be seen that an increase of the cathodic overpotential from 87 to 250 mV results in a decrease of the ductility, even if the fluctuation of the ductility is quite large. It should, however, be emphasized that also crystallographic texture, grain size, and

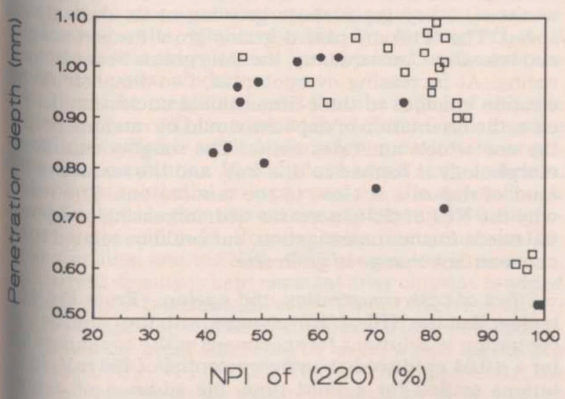


Fig. 9. Effect of NPI of (220) on the ductility for all the specimens with a roughness factor $\alpha < 0.04$. (●) Long settling time, (□) short settling time.

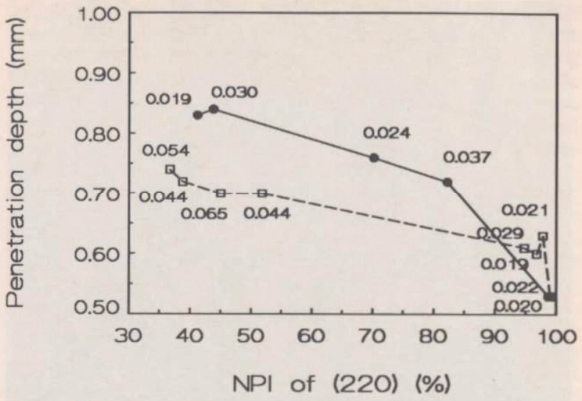


Fig. 10. Effect of NPI of (220) on the ductility of all specimens deposited at an overpotential of 250 mV and 25°C. (●) Long settling time, (□) short settling time. For each measuring point the roughness factor is mentioned.

morphology of electrodeposited metals are quite sensitive to changes of the overpotential. Therefore the variation of ductility with overpotential has to be considered in view of concomitant changes of crystallographic texture, morphology, and grain size.

Overpotential and grain size.—Fairman (21) studied the grain size of copper deposited from an acid copper sulfate solution containing 1.25M $CuSO_4$ and 0.51M H_2SO_4. He reported that at increasing current density from 1.99 to 3.98 A/dm², the grain size became smaller. Since higher current densities require increasing cathodic overpotentials, this means that the grain size decreased at increasing overpotential. The present results are in agreement with those of Fairman: at an overpotential of 113 mV a grain size of 2 μm is noticed (specimen No. 17), at an overpotential of 250 mV the grain size was 1 μm (specimen No. 32) (Fig. 12).

The grain-size dependence of ductility is not well documented in the literature (7). Carreker and Hibbard (22) studied the elongation change of rolled and annealed copper with grain size varying from 12 to 90 μm; no apparent effect of grain size on elongation values was observed. They explained this by the fact that the differences of flow stresses between specimens with different grain size become progressively smaller with increasing strain, because coarse-grained specimens strain-harden more rapidly than fine-grained specimens. It then can be concluded that when copper fractures at larger strains, the effect of grain size on the ductility is less important. Lawley and Schuster (23) showed that the elongation of 99.995% purity rolled copper decreased from 12.5 to 10.7% when the grain size was increased from a fine grain size (between 5 and 15

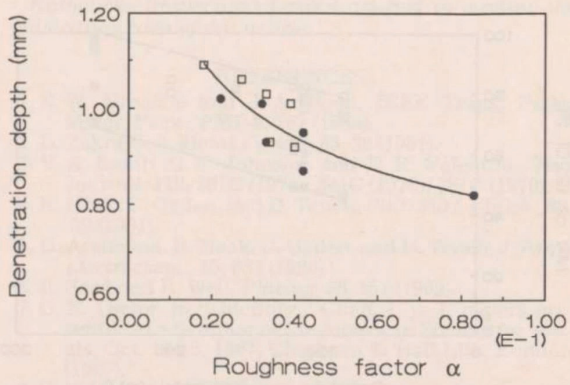


Fig. 11. Effect of roughness factor on the ductility of all specimens deposited at an overpotential of 113 mV and 25°C. (●) Long settling time, (□) short settling time.

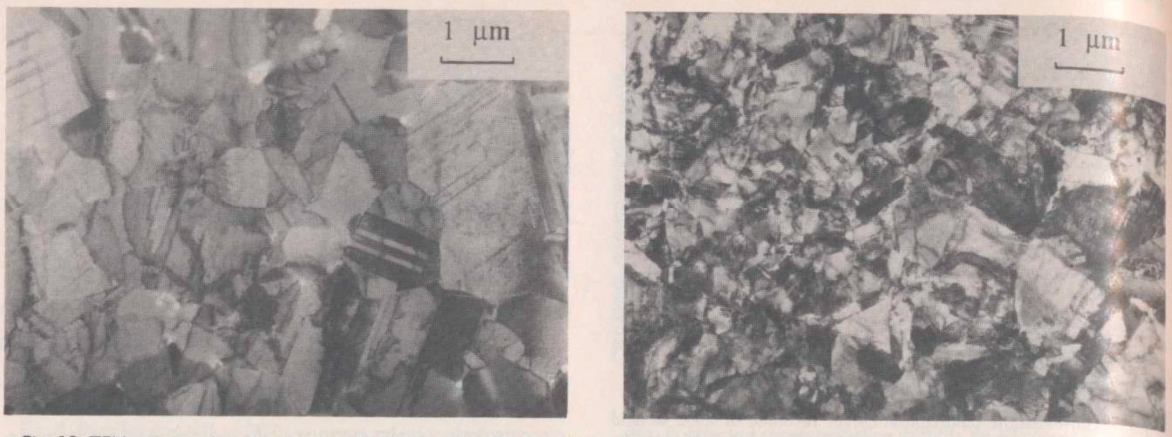


Fig. 12. TEM micrographs of specimens with different ductility and electrodeposited at different overpotentials. (a, left) Specimen No. 17 deposited at an overpotential of 113 mV and 25°C. (b, right) Specimen No. 32 deposited at an overpotential of 250 mV and 25°C.

μm) to a coarse grain size of (130 × 180) μm² for specimens with a thickness of 53 μm. For specimens with a thickness below 26 μm, the ductility increased when the grain size was increased. For instance, the elongation increased from 5.8 to 9.2% when the grain size changed from a fine size (between 5 and 15 μm) to a coarse grain size of (70 × 300) μm² for specimens with a thickness of 6 μm. Recently, Nakahara *et al.* (24) observed that the ductility of fine-grained electroless copper specimens (0.5 to 2 μm) and large-grained specimens (10 to 40 μm) was 0.9 and 16%, respectively. Our results (see Table I) show that the ductility of electrodeposited foils decreases from 1.06 mm (specimen No. 17) to 0.83 mm (specimen No. 32) when the grain size decreases from 2 to 1 μm. According to Nakahara, 2 and 1 μm grain sizes are fine-grained specimens, so it is difficult to conclude that the ductility of copper decreases only due to a change of grain size from 2 to 1 μm. It seems thus that the effect of grain size on ductility is more complicated than the well-documented effect of grain size on yield stress or flow stress and still needs further investigation.

Overpotential and texture.—The NPI of (220) increases with the cathodic overpotential as shown in Fig. 13. In order to eliminate the effect of a high roughness, this relationship was plotted for specimens having a roughness factor α smaller than 0.04.

Bockris and Razumney stated (15) that according to Reddy's postulate (25), out of the ensemble of crystallites which constitute a polycrystalline substrate, a certain number of grains will have an orientation equal to (or close to) the preferred one. These crystallites will have a higher rate of outward growth than the others and will eventually, but not immediately, predominate in determining the surface topography. Obviously, differently oriented grains of

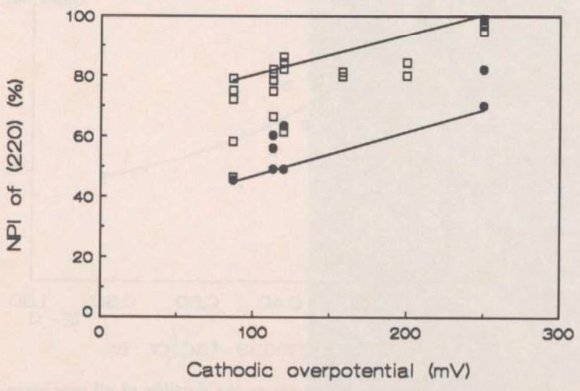


Fig. 13. Relationship between overpotential and texture for all specimens with α <0.04. (●) Long settling time, (□) short settling time.

polycrystalline metallic electrodeposits have different growth rates at a given overpotential. If the electron charge transfer is the controlling step for the cathodic reaction, according to the Butler-Volmer equation, for every individual (hkl) facet the current density can be expressed as follows

$$i_{k(hkl)} = i_{0(hkl)} \exp(\beta\eta F/RT) \quad [2]$$

where β is the symmetry factor and η is the overpotential. So if β and η are independent of the grain orientation, the grain with the highest exchange current density grows fastest, and the grain with the lowest exchange current density grows slowest.

Damjanovic *et al.* (26) determined that in acid copper sulfate solutions $i_{0(110)} > i_{0(100)} > i_{0(111)}$, and that $i_{0(110)}/i_{0(111)} = 5$. So grains with a (110) plane parallel to the electrode surface grow five times as fast as grains with a (111) plane do at the same overpotential. Earlier experiments performed by Storey and Barnes (27) support this hypothesis. They reported that surfaces near (100) had received more than the average amount of deposit, while grains with a surface near (111) received considerably less than the average amount deposited. It can be seen from their data that the surface parallel to a (110) plane also had received more than the average amount of deposit. Our results are in agreement with those of Storey *et al.* and Damjanovic *et al.*

According to Winand's hypothesis (28), the type of nucleation changes from two-dimensional nucleation to three-dimensional nucleation with increasing ratio i/i_{dl} of the apparent current density i to the diffusion limiting current density i_{dl}. When $i << i_{dl}$, grains grow in a two-dimensional fashion. At first, various grains grow epitaxially on the substrate surface. While the influence of the substrate weakens, every grain starts growing at its own growth speed. The (110) orientated grains grow faster outwards and laterally. Consequently, the (110) grains become dominating. At increasing overpotential, two-dimensional nucleation changes to three-dimensional nucleation. In this case, the orientation of deposits would be random, or form the one which nucleates easier. The rougher cauliflower morphology is formed in this way, and the texture of this kind of deposits is close to the random one. The reason why the NPI of (220) increases with increasing overpotential needs further investigation, but could be related to the concomitant change in grain size.

Effect of bath composition and ageing.—From Fig. 14 it is clear that the NPI of (220) changes with the chloride concentration in solutions for specimens with a roughness factor α <0.04 produced at an overpotential of 250 mV. In solutions settled for a short time, the addition of a small amount of chloride has a dramatic effect creating a strong (220) texture. That (220) texture increases with Cl^-. The effect of a chloride addition to solutions settled for a long

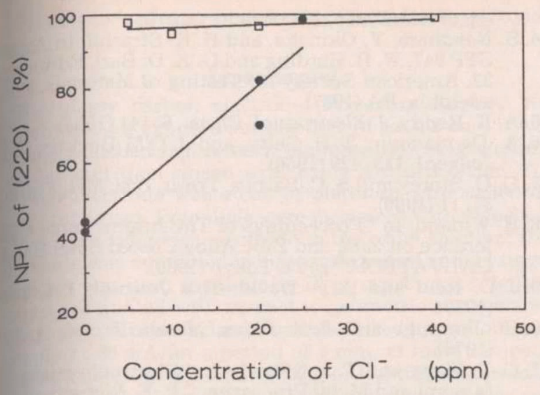


Fig. 14. Effect of chloride concentration on NPI of (220) for specimens with $\alpha < 0.04$ and electrodeposited at 250 mV. (●) Long settling time, (□) short settling time.

time is, as a general trend, that a (220) texture develops with increasing Cl^- content. This trend can also be found for deposits produced at other overpotentials, for instance, in the group of deposits produced at 120 mV.

A polarization curve in a chloride-free solution containing $0.36M$ $CuSO_4 \cdot 5H_2O$ and $2.04M$ H_2SO_4 is plotted in Fig. 7. The present result is in agreement with Reid and David (29) who measured the steady-state cathodic polarization curves on a RDE in an acid solution containing $0.24M$ $CuSO_4$ and $1.8M$ H_2SO_4 at rotation speeds varying from 0 to 500 rpm.

Chloride ions have a depolarizing effect on the cathodic copper deposition (Fig. 7). There are different effects of chloride ions on the cathodic polarization reported in literature. Jennings *et al.* (30) reported that Cl^- was a depolarizer, if the concentration of Cl^- was not larger than $8.6 \cdot 10^{-3}M$ in a solution containing $0.55M$ $CuSO_4 \cdot 5H_2O$ and $0.80M$ H_2SO_4. When the concentration of the salt was larger than $8.6 \cdot 10^{-3}M$, they observed the polarizing effect of the chloride because of the precipitation of the cuprous chloride. Lakshmanan *et al.* (18) reported that for a solution containing $0.32M$ Cu^{++} and $1.53M$ H_2SO_4 at 35°C, chloride ion up to 10 ppm depolarized the cathode reaction, and that on the contrary, above 40 ppm chloride ions have a polarizing effect. They considered that the polarization was caused by the precipitation of cuprous chloride, when its solubility limit was reached by having added above 10 ppm of Cl^- to the solution. But Wang and O'Keefe (31) found that for a solution containing $0.57M$ Cu^{++} and $1.65M$ H_2SO_4 at 40°C, the chloride ion polarized at a low concentration of 5 ppm and depolarized at higher concentrations of 20 to 40 ppm. It appears that the effect of the chloride on the cathodic polarization curve is complicated. These contradictory results may be caused by different methods of measuring the polarization curves. Further investigation is necessary to give a satisfactory explanation for these contradictory results. Obviously, the depolarizing effect of chloride in this study cannot be explained by the precipitation of cuprous chloride.

It should be mentioned here that the effect of chloride on the texture will be completely different, whether the electrodeposition is carried out under potentiostatic or galvanostatic conditions. If chloride is added to the solution, and the overpotential is kept constant, the deposition is carried out at a higher current density because of the depolarization by chloride. Consequently, the grain size becomes smaller, and the NPI of (220) increases. If, however, the current density is kept constant after chloride is added to the bath, as Lakshmanan *et al.* (18) or O'Keefe *et al.* (17) did, the deposition will be carried out at a lower overpotential, hence the grain size could be larger which results in a decrease of the NPI of (220). That is why, apparently, the effect of chloride on the texture obtained by those authors was different from that observed in this study.

Another effect of chloride is that it smoothens the copper coatings. From Table I it can be seen that most specimens with a roughness factor $\alpha \geq 0.040$ were deposited from solutions containing less than 5 ppm Cl^-. That smooth deposits are preferentially formed in presence of chlorides is in agreement with the observation by Knuutila (32). On the other hand, an excess of chloride ions has a negative effect on the ductility, and all coatings deposited from a solution containing 85 ppm chloride ions are porous (9).

Another factor which influences the ductility is the bath ageing time. Deposits produced from solutions aged for a different time have different structure characteristics and, hence, different ductility, even if the other conditions are the same. The ductility of specimens in group L is generally lower than that in group S (Fig. 9). The reason why different settling times affect the ductility and the texture still needs to be investigated. Possible reasons can be an effect of oxygen in the solution or an effect of a different concentration of cuprous ion.

Conclusion

1. In the present study ductility of copper foils was measured under a biaxial stress state. In order to describe the crystallographic texture of these coatings, it was shown that preference should be given to normalize it with respect to a randomly oriented powder sample.

2. Concerning the correlation between processing parameters, structure of deposits, and ductility, the cathodic overpotential was found to be the determining processing parameter. An increasing overpotential leads to a crystallographic texture change of the specimen. The normalized peak intensity of (220) orientation increases with the cathodic overpotential. A further increase of the overpotential can induce a three-dimensional nucleation, and the surface of deposits becomes rougher. In this case, the texture of specimens is close to the random one. A decrease of the grain size is also observed at incresing overpotential.

3. The crystallographic texture of copper layers strongly influences the ductility. Specimens with a higher normalized peak intensity of the (220) orientation have a smaller plane strain flow stress to balanced biaxial flow stress value and lower ductility.

4. The initial surface irregularity of a specimen influences its ductility. Specimens with a higher roughness factor obtained by increasing the roughness are less ductile.

5. Adding chloride to the bath leads to a higher normalized peak intensity of (220) and a smaller roughness, if the chloride concentration is lower than 40 ppm.

6. The ageing of plating baths is another factor which influences the ductility. Smoother copper deposits obtained from a solution settled for less than 3 h between two successive tests, have a little higher ductility than those deposited from a solution settled for a long time.

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Generation of Hydrous Oxide Species at Carbon-Supported, Finely Divided Platinum Surfaces

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ABSTRACT

It has been pointed out recently that with regard to the electrocatalytic behavior of noble metal electrodes, the important species in a number of technologically important processes are submonolayer coverages of hydrous oxide species; these may inhibit certain reduction processes or accelerate certain oxidation reactions. It was demonstrated in the present work that such an oxide can be generated more readily on carbon-supported, as compared with platinum-supported, platinum black deposits. Thick films of the hydrous oxide formed on platinum were found to be relatively stable, *e.g.*, they were resistant to reduction to potentials below that at which the normal monolayer oxide was reduced. Their inhibiting effect on the oxygen gas reduction processes was demonstrated. It is suggested that such species are produced at submonolayer coverages at active, adatom sites at much lower potentials where they enhance certain anodic processes, *e.g.*, methanol oxidation, but inhibit certain cathodic processes, *e.g.*, oxygen gas reduction. The latter reaction at potentials of interest in fuel cell work, 0.8 to 0.6 V (RHE), may be forced to occur at less active sites on the surface where incipient hydrous oxide formation is less likely to occur.

Due to its high catalytic activity and marked resistance to corrosion, platinum is often the metal of choice both for fundamental investigations and technological applications in electrochemistry. For many applications in the latter area the metal is employed in a finely divided form on a conducting support, usually some form of carbon; this reduces the cost associated with the use of a noble metal. The metal itself is frequently employed in fundamental investigations of anodic oxidation processes, both of the surface itself (1, 2) and also the reaction at the latter of organic species of interest in electro-organic synthesis, electroanalysis, or fuel cell systems (3). A common feature in many investigations in the latter area is the emphasis on only one of two possible products of platinum oxidation, namely the monolayer-type product which is frequently represented as OH_{ads} or O_{ads}; due to place-exchange reactions at significant coverage such deposits may acquire some of the character of a phase oxide. However, there is an alternate, though frequently ignored, product of platinum oxidation in aqueous media, namely the hydrous oxide, originally represented as $PtO_2 \cdot nH_2O$ (4) or, more recently (5, 6), as a hydrated form of insoluble platinic acid, $H_2Pt(OH)_6$, or, in solutions of high pH, an agglomerate of the anionic form of the latter. An account of the electrochemistry of hydrous oxides of platinum and various other metals was published in a recent review (7); the relevance of such species, both as mediators of oxidation processes (2) and inhibitors of reduction processes (2, 8), was pointed out recently.

The techniques usually employed to generate thick hydrous oxide films on platinum (7) entail the use of high anodic potentials; even the use of a potential cycling technique (5), involves the application of a high anodic limit. However, it has been pointed out (2, 8) that quite low coverage, submonolayer, deposits of such species apparently form spontaneously at quite low potentials, 0.2-0.6 V(RHE), at adatom sites on the electrode surface. It was observed recently (9) that such species form more readily under the rather severe conditions encountered in fuel cell systems, *e.g.*, in 3.0 mol dm^{-3} H_2SO_4 at 60°C in the case of the methanol/air fuel cell. The redox behavior of the premonolayer metal oxide, in the case of finely divided platinum on carbon, *i.e.* a fuel cell electrode, cannot be easily investigated as the large capacitative (and pseudocapacitative) response of the high surface area carbon masks the low level response due to the adatom/hydrous oxide transition of the metal. To study the latter reaction we have investigated the behavior of the finely divided metal, *i.e.*, platinum black, on a glassy carbon substrate. The results demonstrate that finely divided platinum is more readily converted to the hydrous oxide when the support is carbon, as opposed to bulk platinum; it was also shown that significant deposits of the hydrous oxide are more inhibiting, *i.e.* lower the onset potential for dissolved oxygen gas

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