Control of Anisotropism for Electroplated Parts of Complex Shape

Craig Bishop, Agnes Rousseau
Atotech USA

It is well known that most electrodeposits are highly anisotropic possessing strong fiber texture. It is also well known that control of anisotropism is of benefit since the crystallographic texture affects properties of crystalline materials. For complex shapes obtaining uniform texture over a variety of current densities and over potential regions is very difficult. Consequently, strip plating has been the primary beneficiary of controlled anisotropism for the past several decades. In this paper we will describe zinc (hexagonal), zinc nickel and chromium (body centered cubic), iron (face centered cubic) and iron phosphorous alloy coating processes that produce uniform texture on complex shapes and discuss the merits and disadvantages of crystalline electrodeposits.

Introduction and Background:

The metallurgical properties of electrodeposited and chemically derived (ECD) elements and alloys often vary significantly from similar pyrometallurgically derived (PyMD) elements and alloys. Despite the variations of ECD vs. PyMD metals and alloys electrodeposition and chemical deposition are important commercial endeavors allowing high throughput, cost effective coating of conductive and non conductive surfaces as well as production of alloys not easily obtained by pyrocrystallization, powder, and vapor metallurgical methods. It also seems that expansion of commercial development in electrodeposition and chemical deposition accompanies development of technology that brings control of the metallurgical properties of the deposits.

ECD metals and alloys can possess unique compositions with mixtures of very dissimilar melting point component elements often achievable, as well as multilayer and 'incommensurate' (period between regular structures varies) structures. With .ECD alloys it is often noted that phases that should be present in pyrometallurgical alloys at specific elemental ratios are not observed with the ECD alloy[1]. That is the ECD alloy is often not in thermodynamic equilibrium generally with expected phases absent and can be considered metastable. In many cases the ECD alloy may not be crystalline at all and considered amorphous and glassy. In some instances subtle compositional differences, resulting in an inadvertent alloy, have been used to explain the variations[ibid]; for example, hydrogen codeposition with chromium or with ZnNi. In other cases variations in lattice constant[ibid] have been used to explain observed variations between ECD and PyMD.

With crystalline electrodeposits the size of the grains are generally much smaller than PyMD grains and grain size can effect hardness with hardness increasing as grain size decreases, the Hall-Petch effect, until grain size is so small that hardness begins to decrease in the inverse Hall-Petch region.

In addition to the preceding ECD metals and alloys often are anisotropic. They will exhibit different properties when tested along axes in different directions. This is due to the grains of the crystalline electrodeposit having non-random preferred crystallographic orientation, also referred to as texture.

---

[1] E. Raub and K. Müller, "Fundamentals of Metal Deposition", 1967, Elsevier, New York, NY; pp. 138-149.

Table 1 Properties of crystals affected by texture (taken from J.E. Nye, Physical Properties of Crystals, 1985 ed., Oxford Press).

- Scalar:
  - Heat capacity
  - BCC hardness
- First rank tensor, a scalar and a vector:
  - Pyroelectricity
  - Electrocaloric effect
  - Heat of polarization
  - Field due to temperature chage
  - Polarization by hydrostatic pressure
- Second-rank tensor relating two vectors:
  - Permittivity
    - [dielectric impermeability]
  - Dielectric susceptibility
  - Permeability
  - Magnetic susceptibility
  - Electrical conductivity
  - Thermal conductivity
    - [thermal resistivity]
  - Thermoelectricity
- Second-rank tensor relating a scalar and a second-rank tensor:
  - Thermal expansion
  - Piezocaloric effect
  - Thermal pressure
  - Heat of deformation
  - Strain by hydrostatic pressure
  - Peltier coefficients
- Third-rank tensor relating a vector and a second-rank tensor:
  - Direct piezoelectric effect
  - Converse piezoelectric effect
  - Piezoelectric effect
  - Electro-optical effect
- Fourth-rank tensor relating two second-rank tensors:
  - Elastic compliances
    - [elastic stiffness]
  - Elasto-optical coefficients
  - Piezo-optical coefficients
  - Electrostriction
- Axial second-rank given the variation of pseudo-scalar with direction:
  - Optical activity
- Other:
  Self diffusion, pyromagnetism and piezomagnetism, magnetostriction, pressure and conductivity, second-order elastic coefficients.

The properties affected by crystallographic orientation are numerous. Detailed reviews on the subject such as Kocks et al.[2] are prepared and there is an international conference devoted to the study of texture[3]. In Table 1 a list is presented where all properties except those defined by scalar values will be affected by crystal orientation. In addition to this tabulation other, more recognizable properties for surface engineering are affected by crystallographic orientation. Dini[4] reviewed this subject as it relates to electrodeposits and points out that formability, corrosion, etching rates, paint adhesion, contact resistance, magnetic properties, wear resistance, porosity, and recrystallization of electrodeposited and chemically deposited coatings are practically affected by texture. There is considerable interest in the relationship between tin and other 'whiskering' phenomena and texture[5]. The innovation of damascene copper to replace aluminum in electronics applications is dependent upon control of anisotropism[6]. The importance of anisotropism with electrodeposition or chemical deposition and efforts to control anisotropism creates a list of publications that grows on a nearly daily basis.

---

[2] U.F. Kocks, C.N. Tomé, H.-R. Wenk, "Texture and Anisotropy", 1998, Cambridge University Press, Cambridge, UK.

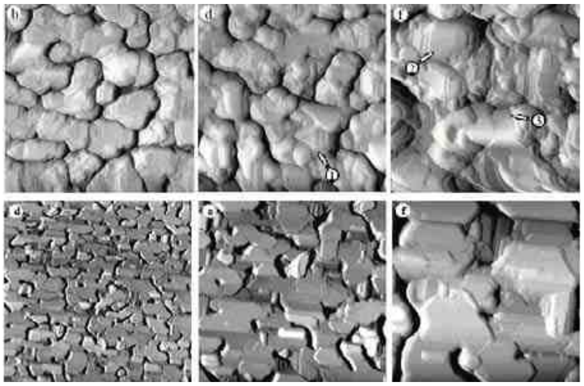
[3] International Committee of Texture of Materials (ICOTOM), http://www.texture-anisotropy.org/

[4] Jack W. Dini, "Electrodeposition, The Materials Science of Coatings and Substrates", 1993, Noyes, Park Ridge, NJ pp. 162-178.

[5] G. T. Galyon, "Annotated Tin Whisker Bibliography," IBM Server Group Chair, NEMI Tin Whisker Modeling Project, July, 2003

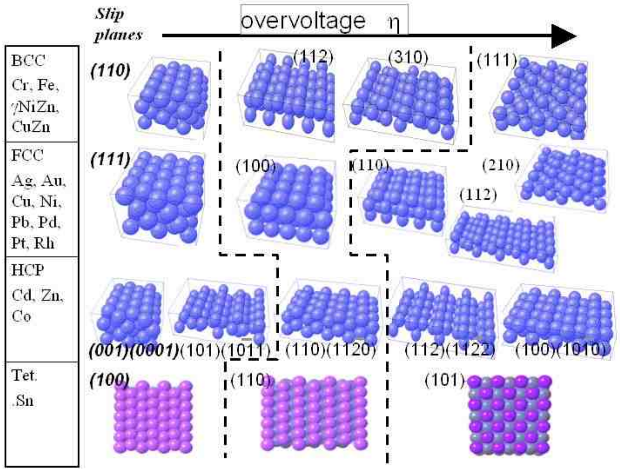
[6] P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, " Damascene Copper Electroplating for Chip Interconnections,", IBM Journal of Research and Development, **42**, 567-574, 1998.

Figure 1 Ultra high vacuum scanning tunneling microscopy of randomly oriented ECD silver grains (top row) and fiber oriented ECD silver grains all on Si(100) (courtesy of Ulrich Memmert, Atotech, Berlin).



As with other comparisons between PyMD and ECD materials typical textures are also different. With PyMD metals texture is usually a result of deformation such as extrusion or rolling and the resulting anisotropism is greatest near the surface and generally asymmetric. With ECD materials texture is generally symmetric about a grain axis with similar crystal planes parallel to the substrate (basal plane) and the 'sides' of the grains randomly aligned. This type of texture is known as fiber texture as it is prevalent with metal and plastic fiber materials typical of composite materials. In figure 1 the surface of randomly oriented electrodeposited silver and fiber oriented electrodeposited silver are examined using scanning tunneling microscopy.

Figure 2 (Miller indexed) dominant planes in fiber oriented ECD metals and alloys from Pangarov[7] with illustrations of the uncontaminated atomic arrangement of their surfaces using Surface Explorer[9].



Complicating all of the above is the fact that current density and or local over potential, as well as additives may affect inadvertent and deliberate alloy composition, phase, crystallinity, grain size, and anisotropism. In particular, anisotropism is affected by over potential, which often accompanies current density variations, as well as by additive. Consequently, it is strip plating and plating of simple shapes, such as cylinders, where current density does not vary greatly on the substrate, that have benefited the most from consistent texture.

Pangarov[7], reviewed reports on electrodeposited metals and their observed texture and developed a very instructive list of typical textures in various electrodeposits as a function of over potential (voltage exceeding minimum voltage for deposition). A variation of this table is given in figure 2. The Miller (and Miller Bravais in the case of hexagonal crystals) orientation notation as a function of over potential among the dominant crystal classes[8] of electrodeposits is presented. We also attempt to illustrate

---

[7] N.A. Pangarov, Prefered orientations in electrodeposited metals. J. Electroanalytical Chemistry **9**, pp 70-85, 1965.

[8] BCC, body centered cubic, FCC, face centered cubic, HCP, hexagonal close packed, Tet, tetragonal.

the atomic density and 'steps' that are associated with uncontaminated surfaces of the principle orientations[9]. The atomic planes with greatest 'areal' density, referred to as 'slip' planes are pointed out. Note, that in every system, slip plane preferred orientation occurs when over potential is minimal. In many studies, slip plane oriented deposits also exhibit the greatest corrosion resistance.

While most electrodeposits tend to follow the over potential observations of Pangarov, with the possible exception of acid electrolyte tin, his data was based upon stannate processes, he also noted that 'adsorbates', that is additives, as well as over potential, could affect ECD metal texture. Consequently, attempts to control ECD texture rely upon a combination of techniques to control over potential and use of additives. Vereecken et al.[10] have pointed out how such strategies can be employed with copper electrodeposits. In general, since 1993, we have attempted to 'control' anisotropism of electrodeposits in much the same manner. We vary the electrolyte and additive in an effort to affect observed orientation with the general principles of higher concentration or conductivity electrolytes and additives that have modest affect on polarization tend to produce lower over potential. We observe orientation primarily by use of x-ray diffraction using Hull cell panels and actual parts of complex shape.

In this paper we will present examples of processes developed to control anisotropism on substrates that have varying current densities due to their complex geometries.

Case Study 1 – Gamma Phase Zinc Nickel from Alkaline Electrolyte:

Early in our development efforts with 'high' (12-17% Ni) alloy zinc nickel we concluded that well document metastability of the electrodeposit presented a challenge. We also concluded from literature dealing primarily with strip plating using acid electrolytes[11] that the bcc gamma phase rather than hcp zinc phase was important for corrosion protection[12]. Consequently our development efforts required extensive structural characterization, usually with x-ray diffraction. The early product from this effort was a deposit that was gamma-phase and possessed extremely strong (600) reflection, which is {100} orientation, over a wide current density range. The consequence of this was a bright but non ductile coating which found commercial success on non flexible parts such as motor housings, and fasteners.
Subsequently, as alkaline high alloy zinc nickel gained commercial importance a more ductile alloy needed to be developed. Colleagues in the United Kingdom, led by Paul Wynn and Lee Capper, experimented with additives and small changes in electrolyte, depositing high alloy onto small tubes that were then bent and examined for cracking. The result of their efforts was a process that became commercially successful.

---

[9] Surface Explorer, found at http://w3.rz-berlin.mpg.de/~rammer/surfexp_prod/SXinput.html
[10] P. M. Vereecken, R. A. Binstead, H. Deligianni, and P. C. Andricacos, " The chemistry of additives in damascene copper plating", IBM Journal of Research and Development, **49**, 1, 2005.
[11] D.E. Hall, *Plating and Surface Finishing*, Nov. 1983, pp. 59
[12] R. Noumi, et al., *SAE*, 1982, 820332

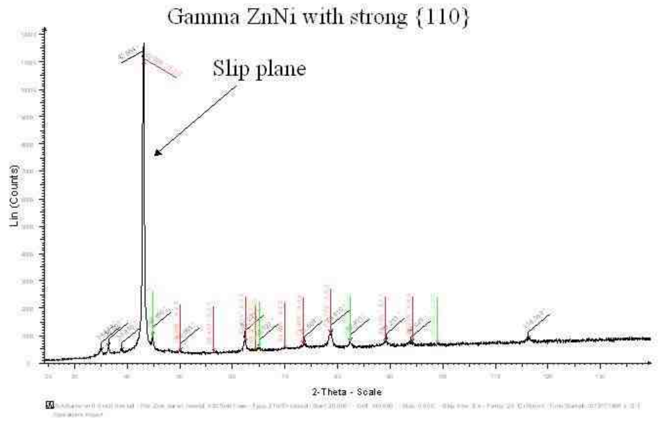


Figure 3 X-ray diffraction data of gamma phase ZnNi with dominant {110} preferred orientation.

While the phase remained gamma phase, a new strong orientation was present, {110}. The orientation was current density specific. Suitable for simple shapes such as unbent tubing when properly jigged.

For material scientists this orientation has significance. The BCC {110} family of planes, are 'slip' planes which when present, parallel to the substrate, allow significant ductility. The slip plane paradigm is that this plane has the greatest density of atoms, or areal density. Corrosion research on single crystal materials indicates that areal density affects not only ductility but also corrosion resistance and adhesion to paint[4]. These observations have led to a barrel plating high alloy zinc nickel process that is {110} oriented and extremely receptive to trivalent passivation and subsequent dip spin or electrophoretic painting (figure 3). Typical corrosion results from this process exceed 100 Ford APGE corrosion cycles[13].

It is important to note that we have not achieved a singleBCC gamma phase {110} zinc nickel electrolyte and additive package effective for all current densities. The high ductility rack process differs in additives from the paint receptive barrel process, and each of these differ from the original, very popular, (600) oriented process which, possesses (600) orientation over a wide current density range. Nontheless, within the practical limitations of barrel plating, or rack plating of simple shaped materials, we have managed to control anisotropism of electrodeposited gamma phase ZnNi.

Case Study 2 – Alkaline zinc electrolytes

Gamma phase zinc nickel is BCC. Zinc, is hexagonal close packed or HCP. We have recently been developing single additive alkaline zinc processes. Single additive systems were very popular in the late 1970's and early 1980's, then gave way to versatile 'mix and match' processes that have additives specific in function, e.g. carrier, LCD brightener, and HCD brightener. The market pendulum began to change back to single additive processes in the late 1990's. And, over the preceding decades the demands on alkaline zinc had changed.

The single additive systems of the 70's and 80's were high luster zinc plating systems with some regard to internal stress and the effect of deposit thickness on material

---

[13] Bishop, et al. "Gamma Phase Zinc Nickel Electrodeposits from Alkaline Electrolyte", SAE_05B_405, Proceeding of the SAE 2004 conference.

properties, but had not emphasized those material property considerations. Typical diffraction data is summarized in figure 4.

Many platers during the 90's, using 'mix and match' processes, sacrificed high luster for low residual stress and ability to routinely achieve reliable thickness of 10, 12 or greater than 15 µm.

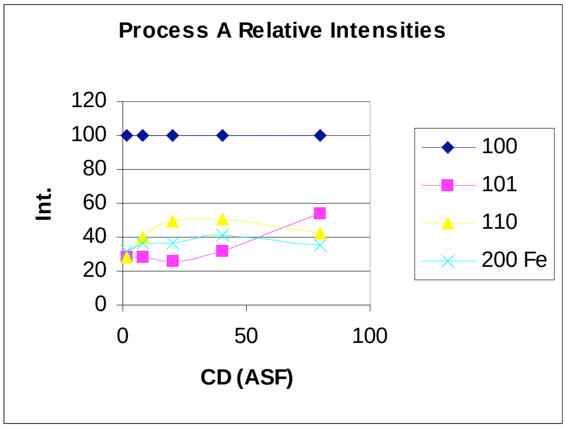


Figure 5 Typical variation in intesity of crystallographic planes in alkaline zinc. (200) Fe is from substrate.

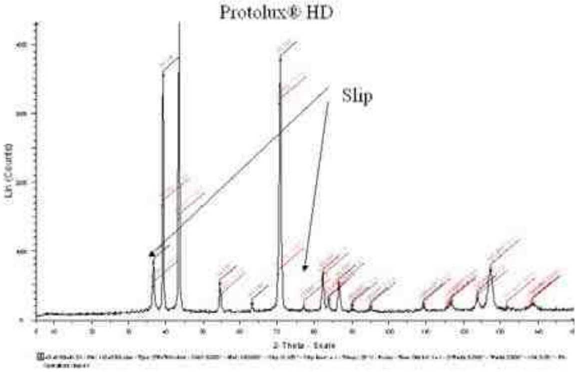


Figure 4 Ensuring presence of {001} slip planes in zinc by XRD.

Surveying the product from such production facilities using x-ray diffraction, we found that the platers tended to evolve their systems toward a preferred zinc orientation on the product that maximized the presence of {001}, in Miller notation, or {0001} slip planes in Miller-Bravais notation[14].

Consequently we developed two single additive systems, one for barrel plating, and another for rack plating. The barrel process emphasized obtaining significant slip plane presence in the deposit. The rack process focused on uniform texture as a function of current density.

The barrel plating process has been in production for nearly two years. The electrolyte is concentrated compared with conventional processes, with the single additive providing significant and reliable {001} orientation. Plating thickness in excess of 20 microns is produced at some production facilities with cathodic plating efficiencies in excess of 80%, sometime approaching 93%. The deposit is resistant to impacts, and possesses 20-30% elongation ductility. An unexpected development has been the ability of the process to plate directly onto high hardness steel; such as metric10.9 property class bolts.

As with many ZnNi applicators, we routinely obtain production samples from applicators using the high ductility barrel zinc process to assess, by XRD, the deposit structure. This program has revealed that over time, parts begin to loose the {001} HCP structure and benefits from this structure. We now have a maintenance program in place that prevents the build up of the materials that created the problem, including cyclic voltametry

---

[14] The HCP crystallographic nomenclature often uses a different nomenclature from the three-integer Miller index nomenclature of other crystal systems. This nomenclature is the four-integer Miller-Bravais index system.

analysis of the solution, and continue to routinely perform XRD analysis on parts from the applicators.

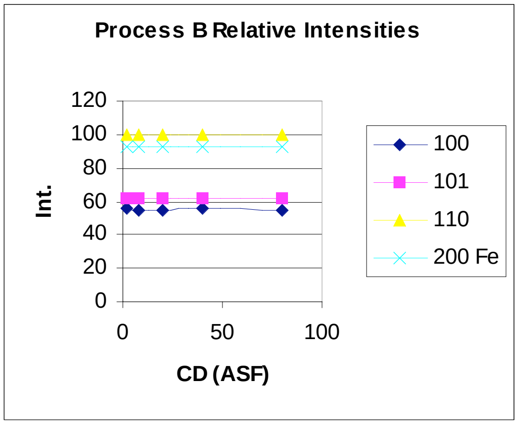


Figure 6 Consistent texture over a wide range of current densities with a new alkaline zinc rack process.

Development of a single additive rack alkaline zinc process is complicated by the fact that most zinc rack plated parts are complex shapes often with deep low current density recesses. Our approach has been to achieve uniform texture over a wide current density range. The process[15], figure 6, achieves uniform texture as a function of current density and is now in beta test with nearly one year of production experience.

Case study 4 – Functional Cr from Cr^{3}

Trivalent solutions of chromium are capable of producing thick chromium deposits. However, these deposits have invariably been amorphous. Over time, or after heating (annealing) the deposit becomes crystalline and volume change results in large cracks, dubbed macrocrack. The chrome obtained from hexavalent solution is typically a very strong {111} texture. The {111} texture is normally associated a higher value for elastic modulus than {100} orientation in BCC materials[16]. However, Cr is unique as a BCC metal, and if single crystal values are used to calculate the predicted modulus ratio for E{111}/E{100} in chromium we find that it is fractional[17]. Therefore we have been working to achieve additive induced crystallization of chromium from trivalent chrome electrolyte as well as ensure that the {111} texture that is present in typical hard chrome deposits is maintained.

There has been progress. Additive induced crystallization has been achieved and we have limited success in creating the {111} orientation. From the Pangarov tables, {111} orientation is associated with high overpotentials. This makes sense for hexavalent electrolyte which has relatively poor cathode efficiencies from 10-25%. Trivalent chromium electrolytes can easily achieve much higher cathodic efficiencies and by deliberately lowering cathodic efficiency of the additive induced process the {111} orientation can be ensured.

Another alternative is to produce a higher efficiency {110} oriented deposit and attempt to requalify the deposit for hard chromium alternatives. Both ideas are being considered

---

[15] Atotech, Protolux® 3200

[16] U.F. Kocks, C.N. Tome, and H.-R. Wenk *Texture and Anisotropy, Preferred Orientation in Polycrystals and their Effect on Materials Properties*, Cambridge University Press, Cambridge, UK, 1998, pp. 237-238.

[17] Craig V. Bishop, Allen Jones, Chris Ringholtz "*Nucleation of Non-conventional Hard Chromium Electrodeposits*", presented at the !Vth International Chromium Colloquium, Saint-Etienne (France) – May 24 – 27, 2004.

as we advance toward commercially viable crystalline chrome from trivalent chromium solution using anisotropism considerations[18].

Conclusions:

Controlling anisotropism of electrodeposits is an important consideration, an opportunity to find new applications for electroplating, and a tool for developing alternative processes to existing processes that may have regulatory issues. The restrictions of overpotential as the determining factor in anisotropism may be manipulated by varying electrolyte and additive. Monitoring of deposits using x-ray diffraction is a useful method of ensuring that anisotropism is controlled.

---

[18] Agnes Rousseau, Zoltan Mathe, Craig Bishop “Direct Current Alternatives for Functional Chromium”, SurFin, 2006, Milwaukee, WI.