Analytically Speaking

Dr. Rolf Weil
Professor Emeritus
Stevens Institute of Technology
Hoboken, NJ 07030

Characterization of Deposits, Coatings & Electroforms, Part 4: Mechanical Properties—Elastic Behavior & Yielding

The last two columns dealt with the mechanical properties and the generalities that apply to most materials. Now the specific aspects applicable to deposits, coatings and electroforms are considered.

Elastic Behavior

The modulus of elasticity, also called Young's modulus, is the property most relevant to elastic behavior. As previously discussed, it is the proportionality constant relating stress to strain. The value of Young's modulus of deposits is generally smaller than that of the same wrought metal. For example, the modulus of electroplated nickel varies, according to Safranek,[1] from 147 to 189 GPa (to convert Pa [pascals] to psi, approximately, multiply by 7). The handbook value for nickel is 210 GPa. Young's modulus, which is determined by the bonds between the atoms, should be structure-insensitive. It should be the same, therefore, for deposits and metals formed by other means.

There are several possible reasons, however, why the moduli of electrodeposits are different. The presence of gas-filled pores, other voids and codeposited organic materials can reduce the load-supporting area. Accordingly, the actual values of the stress and, consequently, the modulus, are larger than those calculated, based on the nominal cross-sectional area. The depth of crevices in the surfaces of thin deposits may also be significant compared to the thickness, and thereby again reduce the load-bearing area locally. As already discussed, clamping thin foils into such devices as bulge testers can cause the elastic limit to be exceeded, so that the actual modulus is not measured. The fact that the modulus varies with the crystallographic direction is not believed to be the reason for the smaller modulus, even though many deposits exhibit a preferred orientation. As discussed earlier, in such deposits, a particular direction is preferentially perpendicular to the surface. The directions lying in the surface in different grains, however, along which the tensile stress is applied, tend to be randomly oriented. In this way, the values of the modulus in different crystallographic directions should be averaged.

The modulus of elasticity of amorphous metals should be larger than that of crystalline ones. The modulus of amorphous electroless deposits is smaller, however. The modulus of electroless nickel containing seven percent phosphorus varies only between 50 and 70 GPa, probably as a result of codeposited hydrogen.

Yielding

It appears that the main factor determining the yield strength of deposits is the grain size. There is an equation, called the Hall-Petch equation, describing the relationship between the yield strength, σ_0, and the grain diameter, D, that many deposits follow,[2-5] which states that

$$\sigma_0 = \sigma_i + kD^{-1/2} \qquad (1)$$

where σ_i is the friction stress representing the overall resistance of the crystal lattice to dislocation movement. The constant k, which has been named the locking parameter, measures the relative contribution of the grain boundaries to strengthening. According to the Hall-Petch relationship, the smaller the grain size, the greater the yield strength.

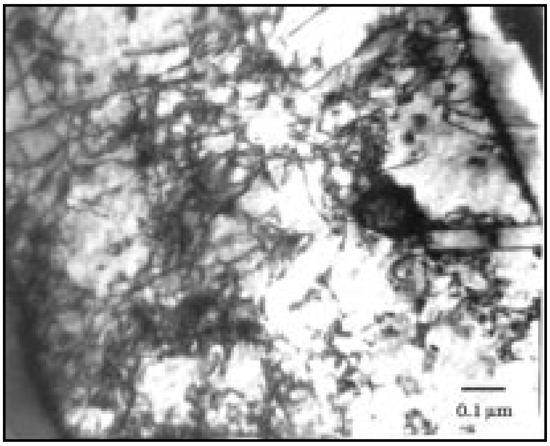

Fig. 1—Transmission electron micrograph showing high dislocation density in a copper deposit.

Deposits tend to have higher values of yield strength than the corresponding annealed metals. The yield strengths of electroplated and wrought nickel, for example, are about 400 MPa and 140 MPa, respectively. The higher dislocation content of deposits is believed to be the reason for a larger value of the friction stress and, consequently, of the yield strength. The high content of dislocations is shown in Fig. 1; the dislocations are the dark lines. The dislocations in deposits are believed to arise from the joining of crystallites to form a layer. If there is a slight misalignment between crystallites, dislocations can compensate for it. As foreign materials tend to segregate in

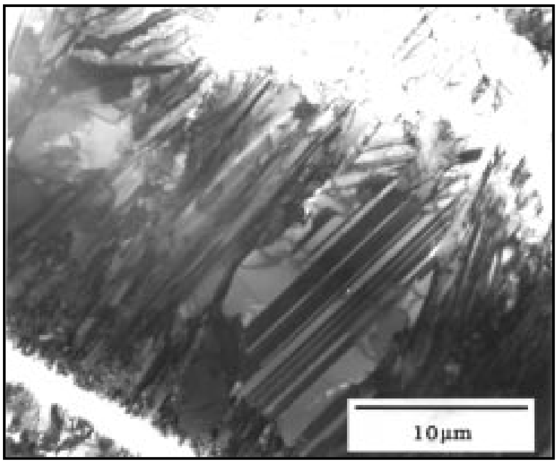

Fig. 2—Transmission electron micrograph of the cross section of a copper electrodeposit showing columnar and equiaxed grains.

the grain boundaries of electrodeposits, the locking parameter would also tend to have a larger value.

The effect of twin boundaries on the yield strength has not been extensively studied. It appears that a smaller spacing of the twin boundaries also results in an increase in the yield strength, but not to the same degree as a fine grain size.

Some electrodeposits exhibit two grain sizes, small and larger. This phenomenon is shown in Fig. 2, which is a transmission electron micrograph of the cross section of a copper deposit. It shows relatively large columnar grains surrounded by small, more equiaxed grains. Both types of grains show many twins that are the sets of parallel lines. Jacobson and Sliwa[4] observed a similar dual grain size in nickel deposits. They modified the Hall-Petch equation by substituting an effective grain diameter D_{eff} for D in Eq. (1). The effective grain diameter was defined as

$$D_{eff}^{1/2} = f_1(D_1)^{1/2} + f_2(D_2)^{1/2} \qquad (2)$$

where f_1 and f_2 are the volume fractions of the small and larger grains, respectively, and D_1 and D_2 are their diameters. By this modification, the data of Jacobson and Sliwa agreed well with that of another study,[2] where there was only one grain size.

It appears that the Hall-Petch equation does not hold when the grain size is less than about 10 nm.[6] It is possible, then, that the volume of the grain boundaries is comparable to that of the grains, and they then dominate. The yield strength then changes only slightly with grain size.[3]

There are several methods for increasing yield strength that are unique to electrodeposits. Dispersion strengthening can be achieved by adding such oxides as those of aluminum or thorium to the plating solution. Stirring the solution so that the oxides are included in the deposits increases the yield strength. An increase of the yield strength of nickel from 245 MPa to 365 MPa has been reported.[7] Periodic reversal of the plating current to form an oxide layer while the deposit is anodic and the subsequent formation of a very fine-grained layer resulted in a yield strength of 900 MPa.[8] Alternate layers of different metals[9] or different phases of the same metal[10] have also been found to increase the yield strength. **P&SF**

References

1. W.H. Safranek, *The Properties of Electrodeposited Metals and Alloys*, 2nd Ed., AESF, Orlando, FL, 1986.
2. B.A. Wilcox & A.H. Clauer, *Acta Met.*, **20**, 743 (1972).
3. A.W. Thompson & H.J. Saxton, *Met. Trans.*, **4**, 1599 (1973).
4. B.E. Jacobson & J.W. Sliwa, *Plat. and Surf. Fin.*, **66**, 42 (Sept. 1979).
5. K. Lin, I. Kim and R. Weil, *ibid.*, **77**, 42 (July 1988).
6. L. Wong, *Nanophase and Nanocrystalline Structures*, R.D. Shull & J.M. Sanchez, Eds., TMS, Warrendale, PA, 1993; p. 85.
7. G.A. Malone, *Plat. and Surf. Fin.*, **68**, 58 (Oct. 1981).
8. W. Kim & R. Weil, *Surf. and Coating Tech.*, **31**, 143 (1987).
9. C. Ogden, *Plat. and Surf. Fin.*, **73**, 130 (May 1986).
10. R. Weil, C.C. Nee & J.W. Chang, *Met. Trans.*, **19A**, 1569 (1988).