Measuring the Elastic Moduli of Electroless Nickel-Phosphorus Deposits

*by Terry Sanderson**

A literature survey showed that reported values of Young's modulus ranged from 48 to 207 GPa (7 to 30 Msi) for high phosphorus (10% or more) electroless nickel (EN) deposits. This wide range seemed physically unrealistic. Moreover, the methods found in the literature for measuring the elastic moduli of metal plating were found to be difficult to use and prone to error. In this work, a simple and reliable way of measuring the elastic moduli of plated metal films is reported, and the Young's and shear moduli of a high phosphorus (10.5%) EN deposit are determined experimentally. It was found that the elastic moduli for the deposit in the as-plated condition, and when baked up to five hours at 190°C (375°F) in air, were essentially constant. The average measured Young's modulus was found to be 114 GPa (16.5 Msi), and the average shear modulus was 42.1 GPa (6.1 Msi). To prove the validity of the measurement technique employed here, the elastic moduli of electrodeposited nickel from a sulfamate bath were also measured, and good agreement was obtained between the measured values and those reported in the literature. The technique presented here is valid for measuring the elastic moduli of any desired metal plating or similar thin film material, and should be of particular value in measuring the properties of brittle deposits like EN.

Electroless nickel-phosphorus (EN) plating has many practical uses, and in applications such as computer hard drives and diamond turned high performance infrared (IR) mirrors, it is critical to hardware performance that the thermal and residual stresses in the deposit be accurately determined. Controlling EN residual stress is also critical to maximizing the corrosion resistance of the deposit. However, stress analyses cannot be undertaken without knowing the elastic moduli of EN. A survey of the literature[1,2] gave reported values of Young's modulus for EN ranging from 48 GPa (7 Msi)[3] to 207 GPa (30 Msi),[4] for what will be called here "high phosphorus" deposits, *i.e.*, deposits with at least 10% P by weight. This wide range seemed physically unrealistic. It was therefore concluded that before EN thermal and residual stresses could be determined, it would first be necessary to measure the Young's and shear moduli, and/or the Poisson's ratio.

Variations in the Young's modulus of EN deposits have been reported for decades, and it has been assumed by some researchers that the variation is due to some thickness dependence in the deposit, and/or possibly substrate effects. This may be true for the very thin EN deposits that are used, for example, in electronic components.[5,6] However, a close consideration of how the Young's modulus is known to vary with plating thickness,[5-7] combined with a review of the property values and measurement techniques that have been reported,[1,2,7,8] would imply a different conclusion for the thicker EN deposits normally used for IR mirrors, computer hard drives and corrosion barrier and wear surfaces.

For crystalline metals as well as EN, the Young's modulus of deposits can differ from bulk metal properties in what will be called here "ultra-thin" plating layers,

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Measuring the mechanical properties of electrodeposits is difficult under any circumstances, but dealing with electroless nickel-phosphorus offers challenges of a higher order. Here, a simpler and more reliable means of measuring the Young's and shear moduli of high phosphorus (10.5%) electroless nickel is presented. Results are compared with sulfamate nickel to confirm the viability of the technique.

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i.e., deposits on the order of several angstroms to perhaps several hundred angstroms thick.[6,7,9-11] Deviation from bulk metal properties may occur in ultra-thin films due to nucleation, epitaxy and pseudomorphology effects, the combination of which may force an ultra-thin deposit to take on an unnatural structure. As the deposit initially nucleates on the substrate, it may exhibit a higher elastic modulus than it would as a bulk metal, because substrate roughness may pin the deposit lattice. However, if this deposit is removed from the substrate, it will no longer manifest the abnormally high elastic modulus. It is also possible for an ultra-thin deposit to exhibit a lower elastic modulus than it would as a bulk metal, which may occur when nucleation sites force an unusual crystal structure on the deposit, or when the density of particular types of defects in the deposit is high. These deposits also usually show a change in modulus if they are disbonded from the substrate.[5-7,9,10]

Ultra-thin metal deposits may, then, exhibit either a higher or lower elastic modulus than they would in bulk form. However, as the deposit thickness grows beyond the ultra-thin range, it tends to assume its own natural structure, upon which the deposit exhibits bulk properties.[6,11] As the ultra-thin layer becomes an increasingly smaller fraction of the total deposit thickness, the contribution of the ultra-thin abnormalities becomes negligible. Deposits for which the contribution of the ultra-thin elastic modulus is negligible will be referred to here as "thick deposits," which are the main interest of this work. Ultra-thin effects should certainly have vanished for deposits of 2.54 μm (0.0001 in.) thickness and greater.[5-7,9,10]

As far as can be found in the literature, for thick deposits, the elastic modulus varies little with deposit thickness. Reports for EN deposits several thousandths of an inch thick show Young's modulus variations of only ±10%.[5] Variations of this magnitude are not uncommon for bulk metals. Furthermore, it can be observed that thick crystalline metal deposits in general may have the same or lower Young's modulus as would the bulk metal form, but not higher.[4,8] For bulk crystalline metals, the one property that usually does not change much with alloying is Young's modulus. However, variations in Young's modulus for commercial nickel alloys vary perhaps more than most common metals, ranging from 179 to 211 GPa (26 to 30.6 Msi).[4] Whether a similar modulus variation obtains for EN is not clear, but the 48 to 207 GPa (7 to 30 Msi) range reported in the literature seems excessive.

It is important to note that the structure of high phosphorus EN is, in the as-plated condition, predominantly amorphous, and as such it is a metallic glass. Metallic glasses are thermodynamically metastable, and in general their properties differ substantially from those of crystalline metals.[18] In certain applications such as diamond turned IR mirrors, EN deposits are used with minimal post-plate baking and are left essentially amorphous. Yet in other applications, such as when EN is used as a wear surface, the deposit may be post-plate baked until it is largely crystallized.[3,12]

The significance of the amorphous as-plated condition of high-phosphorus EN is that the Young's modulus can be expected to show a dependence on the degree of crystallinity, with the amorphous state almost certainly being lower than that of the fully crystallized state. Crystallized EN consists of pure nickel clumps suspended in a nickel phosphide matrix,[13-15] and in the fully crystallized state, we may expect even a high-phosphorus EN deposit to have essentially the same Young's modulus as that of a bulk crystalline nickel alloy. Low-phosphorus EN, in the 2 to 4% P range, is predominantly pure crystalline nickel in the as-plated condition,[13-15] and therefore should also have a Young's modulus similar to that of a bulk crystalline nickel alloy.

Some of the reported Young's modulus variations for EN may be due to the fact that not all references clearly indicate the degree of crystallinity that was measured. Variation may also be related to the fact that obtaining accurate measures on thin metal films is not a simple task. Nonetheless, in the as-plated condition, the Young's modulus of EN should decrease as the phosphorus content increases. How much variation, if any, Young's modulus would show for as-plated high-phosphorus deposits over the 10 to 12.5% P range is not currently known.

Experimental approach

Various methods of measuring Young's modulus and either the shear modulus or Poisson's ratio for metal deposits have been used in the past,[1,2,7,9,10,17,19] including tensile tests on free standing films, inference from the deflection of bimetallic strips, deflection of thin disks subject to a pressure differential, nanoindentation and vibrational resonance methods. However, there are warnings through out the literature regarding the difficulty of obtaining reliable results using all of these methods. Free standing films, for example, are difficult to grip properly in a tensile test machine, require that a strain gage be bonded to the specimen to measure Poisson's ratio, and are prone to tear or fracture at defects along the edges where the specimens are cut. None of the techniques reported in the literature for measuring the elastic moduli of metal plating were deemed suitable for routine engineering purposes, and an alternate technique was sought.

One approach would be to plate both sides of a thin metal strip as shown in Fig. 1, perhaps using a ~2.5 × 15.2 × 0.05 cm (1 × 6 × 0.020 in.) substrate of aluminum, steel or other commonly available metal. The plating would be perhaps 127 μm (0.005 in.) thick on each side, and the plated specimen could be pulled in a tensile test machine. If the Young's modulus of the substrate is known, then the Young's modulus of the deposit could be inferred from the slope of the load deflection line of the plated specimen. A strain gage could be bonded to the specimen to measure Poisson's ratio. To avoid cracking the EN in the grips of the tensile test machine, the ends of the substrate could be masked before plating, leaving the ends of the substrate bare for gripping after plating.

The technique used here, as a matter of convenience, was to plate a cylindrical tensile test specimen similar to what is recommended in ASTM E 8, with 15.88 mm (0.625 in.) diameter ends but with the gage section turned down to a nominal 2.87 mm (0.113 in.) diameter, as shown in Fig. 2. Then a nominal 0.254 mm (0.01 in.) of EN was deposited on the specimen (the deposit thickness measured radially), as indicated in Fig. 2. From the slope of load-deflection and torque-rotation curves, the Young's modulus and shear modulus of the deposit were determined. In all cases, the test specimens were loaded below the expected yield and fracture points of the rod and deposit, given that the failure behavior of the plated rod would probably be too complex to interpret anyway. Keeping all loads below failure allowed the use of the same test specimens to measure both the Young's and shear moduli.

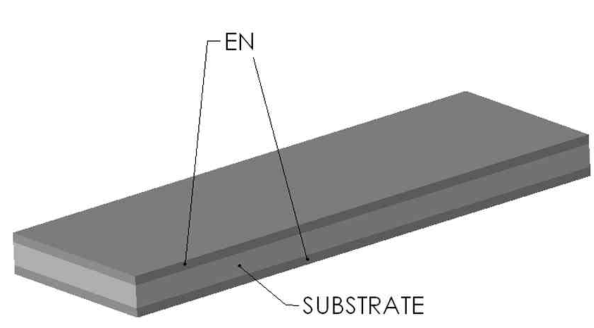

Figure 1—Flat plate specimen for measuring Young's modulus of EN deposit.

Tensile test rods as described above were machined from 5456-H18 aluminum rod stock conforming to MIL-HDBK-5H, the condition -H18 being chosen, because it was readily available. Electroless nickel was plated onto the aluminum test rods using a standard zincate strike layer which was, for current purposes, of negligible thickness. Aluminum was chosen, due to its relatively low elastic moduli, which, it was thought, would make it easier to determine the moduli of the EN experimentally. The EN deposit was to be baked after plating, and 5456 alloy was chosen because, in the annealed condition, it was the strongest of the 5000 and 6000 series aluminums that were readily available.

The simple relationships between load and deformation for a plated test rod are:[16]

$$\delta = \frac{PL}{A_1E_1 + A_2E_2} \tag{1}$$

where δ = elongation,
P = applied load,
L = length of specimen,
A = cross-sectional area and
E = elastic modulus.

$$\phi = \frac{TL}{J_1G_1 + J_2G_2} \tag{2}$$

where ϕ = rotational angle,
T = applied torque,
L = length of specimen,
J = polar moment of inertia and
G = shear modulus.

with "1" subscripts denoting aluminum and "2" subscripts denoting the plating. The stresses in tension are given by:

$$\sigma_1 = \frac{PE_1}{A_1E_1 + A_2E_2}\ ; \qquad \sigma_2 = \frac{PE_2}{A_1E_1 + A_2E_2} \tag{3}$$

while for torsion the maximum shear stresses are:

$$\tau_1 = \frac{T_1r_1}{J_1}\ ; \qquad \tau_2 = \frac{T_2r_2}{J_2} \tag{4}$$

where r is the radius and

$$T_1 = \frac{TG_1J_1}{J_1G_1 + J_2G_2}\ ; \qquad T_2 = \frac{TG_2J_2}{J_1G_1 + J_2G_2} \tag{5}$$

Using MIL-HDBK-5H values for aluminum of E = 70.3 GPa (10.2 Msi) and G = 26.2 GPa (3.8 Msi), graphs of load versus deflection are shown in Figs. 3 and 4, for assumed values of E and G for the electroless nickel. The torsion test equipment used in this work gripped the specimen at the ends, via the slots shown in Fig. 2, and the total specimen rotation angle was measured. Due to the variation in diameter at the ends of the gage section, in order to find G experimentally, it was necessary to solve the following equation:[16]

$$\phi = \int_0^L \frac{T}{J_1G_1 + J_2G_2}dx \tag{6}$$

where x = distance along the length of the test rod, L = plated length indicated in Fig. 2 and J_1 and J_2 are now functions of x. The integral is easily evaluated numerically, and the result was checked against a finite element model. The use of a rotary strain gage could eliminate the need for Equation 6.

In general, the diameter of the test rod, the thickness of the deposit and the test rod metal can be chosen for convenience, depending on the expected modulus of the deposit. Whatever combination renders an easy experimental determination of the deposit properties may be used, the main limitation perhaps being the plating thickness that can practically be deposited. In this work, it was not known in advance what properties the deposit would have, though the moduli of bulk crystalline nickel were expected to be the upper limit.

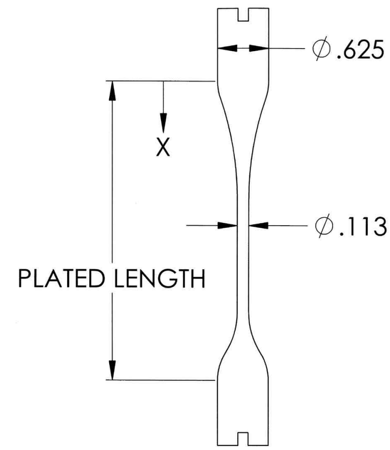

Figure 2—Test specimen geometry, with slots machined in ends for mounting in torsion test machine.

A tensile test machine** was used, which employed a calibrated load cell and an extensometer calibrated to 0.5%, and the output was read by a digital storage oscilloscope. Torsion tests were con-

** *MTS Tensile Test Machine, MTS Systems Corp., Eden Prairie, MN*

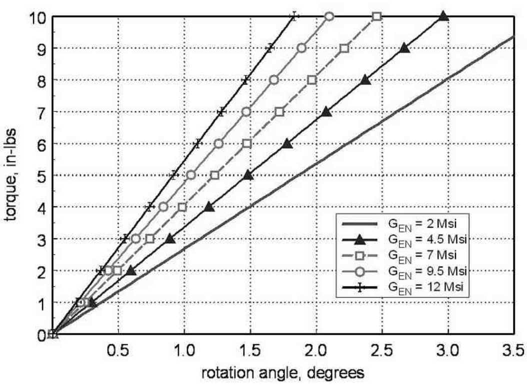

Figure 3—Predicted torque-rotation curves for plated rod, assuming 0.532-in. gage length.

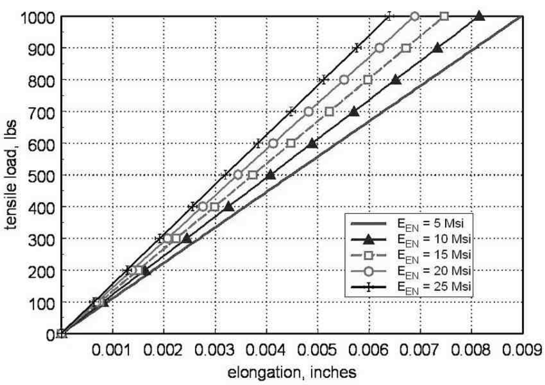

Figure 4—Predicted load-deflection curves for plated rod, assuming 1-in. gage length.

ducted on a test machine capable of providing a zero to 1.13 m·N (zero to 10 in-lb.) torque range and 0.01° steps in rotational angle. The torque test machine is shown in Fig. 5. The machine consisted of a DC stepper motor and torque transducer, which was calibrated immediately prior to use with a 10-inch lever arm and a certified NBS weight set accurate to 1/100 gram. The input and output of the torsion test machine were connected to a personal computer.

Results

Electroless nickel was plated on the test rods with a nominal 10.5% phosphorus content, and phosphorus measurements of the deposit showed a ±0.4% variation. Methods described in ISO 4527 and ASTM E 156-88 were used to measure the phosphorus content, and good agreement was obtained with both methods. A total of 60 specimens were EN plated to a nominal radial thickness of 0.25 mm (0.01 in.). The diameter of all specimens was measured before and after plating at three locations, and computed averages were used in conjunction with Equations 1 and 6 to determine the elastic moduli. Ten specimens each were tested in the as-plated condition, as well as after baking for 1, 2, 3, 4 and 5 hr at 190°C (375° F) in air. These bake times and temperatures are appropriate for when a thermally stable but amorphous deposit is needed in the end product, such as might be used to achieve maximum corrosion resistance, or to produce a diamond turned IR mirror.

Representative tensile and torsion test results are shown in Figs. 6 and 7, from which the Young's and shear moduli were determined using Equations 1, 2 and 6. No statistically significant difference in elastic moduli was found between the as-plated and baked EN samples, implying that no significant amount of crystallization occurred during the bake. The measured shear modulus was G = 42.1 GPa (6.1 Msi), with a range of 39.3 to 49.0 GPa (5.7 to 7.1 Msi) and a standard deviation of 4.8 GPa (0.7 Msi). The Young's modulus measurements yielded an average E = 114.0 GPa (16.5 Msi), with a range of 95.8 to 126.0 GPa (13.9 to 18.3 Msi) and a standard deviation of 12.4 GPa (1.8 Msi). Because no difference was found between the as-plated and baked specimens, the results given here are based on a sample size of 60. The Young's modulus measured here agrees well with the as-plated value of 110.0 GPa (16.0 Msi) reported by Killpatrick[1] for a deposit with 11 to 13% P, who gave a corresponding Poisson's ratio of 0.41 for the same deposit. The average moduli measured here gave a Poisson's ratio of 0.35.

For the EN tensile test result shown in Fig. 7, on the initial portion of the load-deflection curve (near zero), a slight irregularity can be seen. The load-deflection curve in Fig. 7 represented the very first time the test specimen was loaded. Similar results have often been obtained by other researchers,[7] and while the cause is not known precisely, it is believed to be due to some relaxation or fracturing of defects at the deposit-substrate interface. Subsequent load cycles beyond the first generally do not exhibit the early irregularity shown in Fig. 7.

In order to further validate the EN measurements, ten aluminum test rods were electroplated with sulfamate nickel to the same 0.25 mm (0.01 in.) nominal thickness. The Young's modulus of electrodeposited nickel from sulfamate baths reportedly exhibits a range of values, from 147 to 207 GPa (21.3 to 30 Msi),[8] but no corresponding value of shear modulus or Poisson's ratio was found in the literature. The Young's modulus measured in this work was E = 191 GPa (27.7 Msi), with a range of 181 to 209 GPa (26.2 to 30.3 Msi) and a standard deviation of 11.0 GPa (1.6 Msi). The shear modulus was measured to be G = 74.5 GPa (10.8 Msi), with a range of 70.3 to 82.7 GPa (10.2 to 12.0 Msi) and a standard deviation of 5.0 GPa (0.73 Msi). The resulting Poisson's ratio was 0.28. The Young's modulus measured here fell within the reported range of values for sulfamate nickel,[8] and the Poisson's ratio and shear modulus agreed well with reported values for bulk nickel.[4]

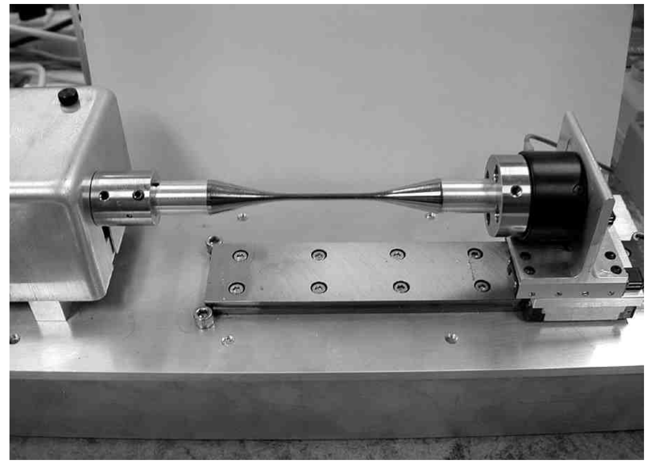

Figure 5—Torsion test machine.

Five aluminum test rods were tensile and torque tested prior to plating, and it was found that the measured Young's modulus agreed with the MIL-HDBK-5H reported value within ±10%, while the shear modulus agreed within ±16%. Perhaps some of the scatter in the measured data could have been reduced if each test rod had been measured and the results recorded, both before and after plating.

Attempts were then made to measure the Young's modulus of free standing films, for both the EN and the sulfamate nickel. Electroless and sulfamate nickel films were made by plating onto

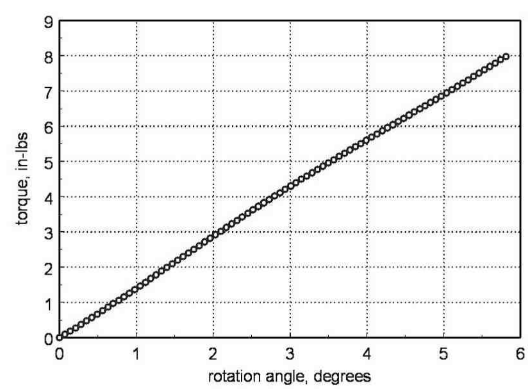

Figure 6—Typical measured torque-rotation curve for EN plated rod. Experimental gage length was effectively the entire specimen length, see Fig. 1.

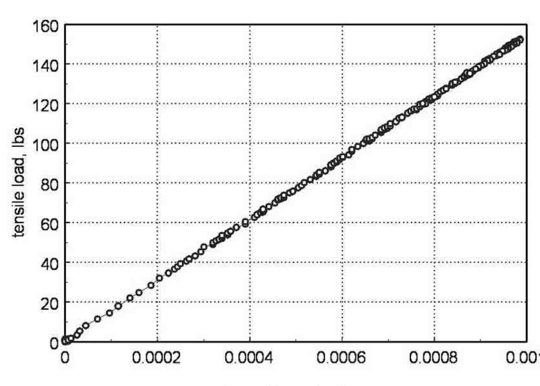

Figure 7—Typical measured tensile load-deflection curve for EN plated rod, 0.25-in. experimental gage length, first loading of specimen shown.

316 stainless steel with no surface preparation to promote adhesion, after which the films could easily be peeled off the substrate. Representative tensile test results for sulfamate nickel are shown in Fig. 8, where values of Young's modulus of 183 and 190 GPa (26.5 and 27.6 Msi) were obtained, in good agreement with the test rod results.

Sulfamate nickel is highly ductile, and premature specimen failure was not a problem for the free standing sulfamate nickel films. On the other hand, no satisfactory measure of Young's modulus was obtained for free standing EN films. The free standing films curled when peeled off the 316 CRES substrate, and often the EN films fractured before any useful data could be obtained, either at the specimen grips or along the edges where the specimens were cut. With great care, attempts were made to cut the specimen edges and reduce the clamping force at the grips to prevent premature fracture, but the EN specimens then slipped in the tensile test machine grips and rendered the measurements useless. Attempts to work with EN films of varying thicknesses did not alleviate these problems. While it was believed that with further effort, results may still have been obtained from the free standing EN films, this avenue was abandoned because it had already demanded far more effort than the test rods. The results from the sulfamate nickel tests were taken as sufficient validation that the experimental technique used here gave an accurate measure for the electroless nickel.

From a practical standpoint, the gage section diameter of the test rod would probably have to be kept small in order to measure the properties of any given metal plating. It was expected in this work that the test rods would be fragile due to the small diameter gage section used. There was concern that the specimens might break or the EN might crack before test data could be obtained. Still, none of the specimens failed prematurely, and all were successfully used to measure both the Young's and shear moduli. Care in specimen handling was required, but it was not prohibitive. The small diameter of the gage section was somewhat difficult to machine but not impossible, and machinability could have been improved by using a harder grade of 5456 aluminum stock. Overall, the difficulties encountered with the test rods used here are believed to be less than what would be encountered using other techniques reported in the literature.

Conclusions

A simple and reliable technique for measuring the mechanical properties of metal plating has been presented and experimentally validated. The technique was used to measure the Young's and shear moduli of EN with a nominal 10.5% P content, giving an average Young's modulus of 114 GPa (16.5 Msi) and an average shear modulus of 42.1 GPa (6.1 Msi). No variation in the elastic moduli were found between as-plated EN, and EN baked at up to 5 hr at 190°C (375°F) in air. Test specimens similar to those used in this work could be used to measure the elastic moduli of any desired metal plating, or other similar thin film material.

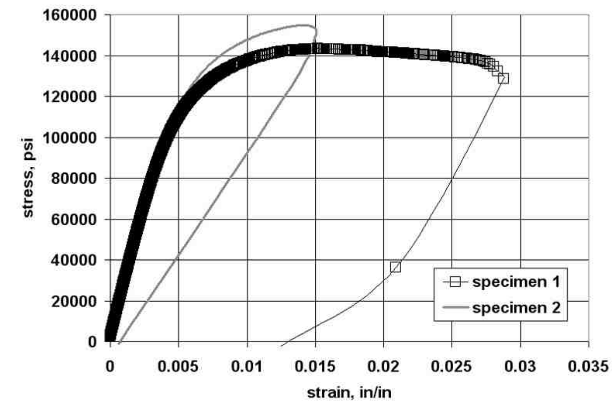

Figure 8—Stress-strain curves for 25.4 µm (0.001 in.) thick free standing sulfamate nickel films (Specimens were not loaded all the way to failure.).

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