



# The William Blum Lectures

#07 - Harold J. Read - 1966



**The 7<sup>th</sup> William Blum Lecture  
Presented at the 53<sup>rd</sup> AES Annual Convention in Miami Beach, Florida,  
June 20, 1966**

**Metallurgical Aspects of Electrodeposits  
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Recipient of the 1965 AES Scientific Achievement Award**





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### Metallurgical Aspects of Electrodeposits

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**Editor's Note:** Originally published as H.J. Read, *Plating*, 54 (1), 33-42 (1967), this article is a re-publication of the 7<sup>th</sup> William Blum Lecture, presented at the 53<sup>rd</sup> AES Annual Convention in Miami Beach, Florida, on June 20, 1966.

#### ABSTRACT

*Experimental studies by many investigators, particularly in the last two decades, have shown that electrodeposited metals and alloys exhibit a remarkable range of metallurgical properties, depending on the bath composition and the plating conditions. Frequently the relationships between the properties are not those commonly observed in materials prepared in other ways. This is a circumstance upon which electroplaters should capitalize, particularly in electroforming, where the significance of metallurgical properties is more readily recognized and more widely appreciated than in decorative and protective plating. But metallurgy is important here also, for fine structure and microtopography are surely intimately connected with appearance of deposits and probably with corrosion resistance.*

It has been my good fortune to have known Dr. William Blum, for whom this Lecture is named, for some 30 years. No great perspicacity on my part was required to recognize him as a scientist and a gentleman at our first meeting. Over the years, I have discovered no reason to change my first impression, and I have found what he has had to say and what he has written sources of continuing inspiration.

Of particular significance to me has been the early recognition by Dr. Blum of the importance of studying the metallurgical structures and properties of electrodeposited metals and alloys. Some of his papers in the 1920s and early 30s presaged the investigations of the last three decades that have shown the remarkable range of structures and properties that can be achieved by electrodepositing a given metal in a variety of ways. In this lecture I shall try to summarize some of the findings that lead me to make this statement.

Most of the work to be described here has been carried out by students as thesis investigations for advanced degrees. I have been fortunate in having a considerable number of such students, and I only regret that I could not find space in the time allotted for the lecture to include some item contributed by each and every one of them. To all of them, however, must go my sincere appreciation of the contributions they have made toward the publications and activities which are the bases for my selection as a William Blum Lecturer and as a recipient of the AES Scientific Achievement Award.

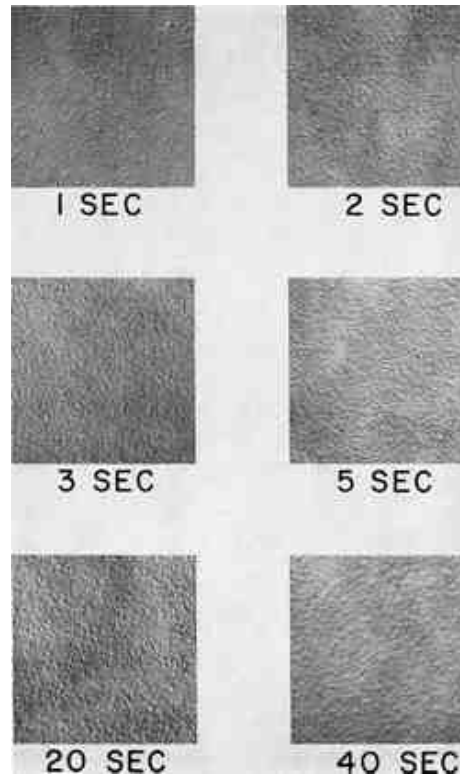
#### Nucleation and growth

Anyone who studies the structure and properties of electrodeposited metals must inevitably at one time or another give some attention to the phenomena of nucleation and growth. Or in other words, how does a deposit get started and then develop to its final thickness and appearance? As an offshoot of some other work on the properties and structure of electrodeposited 70-30 brass, Nystrom and Read<sup>1</sup> have found, not surprisingly, that many factors influence in a striking way the nucleation and growth pattern of this electroplated alloy. The composition of the solution and the nature of the basis metal are, as one would expect, two of the most important variables.

Because the nucleation phenomena, at least in brass, involve very fine structural features that are beyond the limits of resolution for ordinary optical microscopy, the electron microscope had to be used. Both replica and transmission techniques were

employed. Because deposition times of only a few seconds were used, the deposits were very thin. Rather special care as well as no little skill and patience were required in the preparation of specimens for the microscopic observations.

The series of pictures in Fig. 1 shows what happens when 70-30 brass is deposited from a pyrophosphate bath on stainless steel. Coverage of the basis metal by the deposit is very rapid, for even in one second most of the basis metal appears to have been covered. Transmission electron microscopy confirmed this. The nucleation sites must, therefore, be very numerous. As the deposit grew in thickness, the general character of its appearance did not change, although the structural features became somewhat coarser.



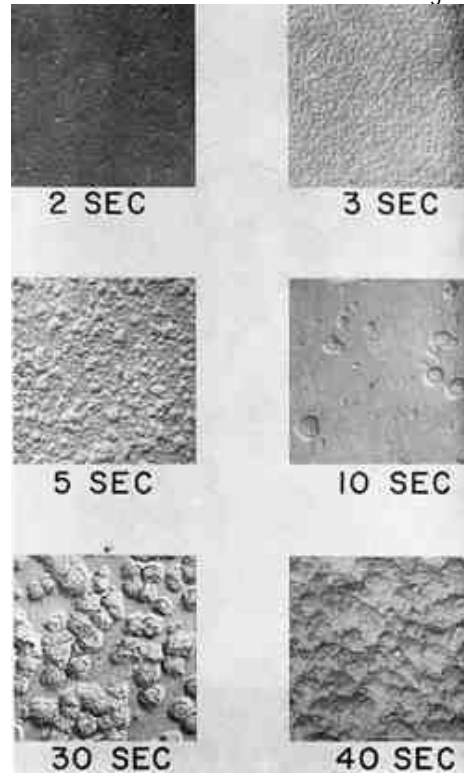
**Figure 1** - Brass with a 70-30 composition deposited from a pyrophosphate bath on stainless steel covers the cathode within 1 sec, and subsequent deposition serves only to coarsen the deposit. Original magnification: 12,500 $\times$ .

A much different course of events was observed when the brass was deposited from a cyanide solution on stainless steel. As appears in Fig. 2, short-time deposits of 2 or 3 sec show a complete coverage of the basis metal. That the coverage was, indeed, complete was established, as for the pyrophosphate deposits, by examination of some specimens by transmission methods. But in the interval between 3 and 5 sec of deposition time, a remarkable change in the character of the deposit occurs. Continuous coverage of the basis metal is no longer found, and the deposit appears to have rearranged itself into isolated clusters or patches! The first time that this was observed, the immediate reaction was that something must have happened to the solution between the plating of the 3- and the 5-sec samples, but additional experiments consistently showed the same apparent rearrangement phenomena.

Although the spaces between clusters in the 5- and 10-sec deposits appear too smooth in the micrographs to represent early uniform deposits on which clusters have developed, this possibility was checked by means of selected-area diffraction examination of the spaces between clusters in specimens prepared for transmission electron microscopy. No sign of metal was found in the spaces. One is forced to accept rearrangement of the deposit as the explanation for the change in its structure.

One of the pitfalls of electron microscopy derives from the high magnification that can be attained. The size of the features observed in micrographs such as those in Fig. 2 is so large that one tends to forget the small actual dimensions that are involved. Thus, it seems, at first sight, impossible that ordinary diffusion along the basis-metal surface of metal already

deposited could account for the rearrangement in a second or so of a continuous coating into isolated clusters. But a calculation based on what seem to be reasonable data for diffusion constants shows that actually one second is enough time for the copper and zinc that comprise the deposit to move half the distance between clusters (the maximum distance that a given atom would have to move). It is much more difficult to support a suggestion that will account for the renucleation that presumably precedes the diffusion process that produces the clusters. Here is an area for some interesting basic research.



**Figure 2** - Brass with a 70-30 composition deposited from a cyanide bath on stainless steel covers the cathode within 2 sec, but after a few seconds, the deposit rearranges itself into isolated clusters, which subsequently grow together to once more cover the cathode. Original magnification: 12,500 $\times$ .

It is evident from this work on brass that, at least for one alloy deposit, there is a marked effect of both the basis metal and the solution on the pattern of nucleation and growth.

### Topographical studies

The electron microscope has been a tremendous boon to those who wish to study the surface structure, that is, the topography of electrodeposits. Because of its enormously better vertical resolution than that of the ordinary light microscope, it is not necessary to flatten or section specimens and one can easily observe the hill-and-dale features that are of interest in topographical studies. A rather long paper by Weil and Read<sup>2</sup> in 1955 showed that wide varieties of topographies were encountered. Both changes in the metal deposited and in the deposition conditions (including bath composition) may produce notable variations in surface structure. Much use has been made of electron microscopy in the last 15 years or so in the study of both properties and behavior of electrodeposits, brightness and corrosion resistance being two areas of special interest.

As examples of topographical studies, some micrographs by Read and Oles<sup>3</sup> are shown in Figs. 3 and 4. They demonstrate quite vividly both that periodic reversal does not always result in surface smoothing or leveling and that an addition agent may profoundly affect the action of periodic reversal in a given plating solution. In this case, the reversal cycles were quite short (in the millisecond range), but in an ordinary Watts bath, there was a notable smoothing action of the current reversal, as can be seen by comparing the dc deposit in Fig. 3 with the pr deposit. The addition of a brightening agent completely reversed the effect of periodic reversal, for now the dc deposit in Fig. 4 is decidedly smoother than the pr deposit. These observations have

significance beyond that of being interesting curiosities. They indicate that whatever may be the mechanism of the brightening action of the addition agent, it involves an adsorption or film-forming phenomenon that cannot be established in a few thousandths of a second.

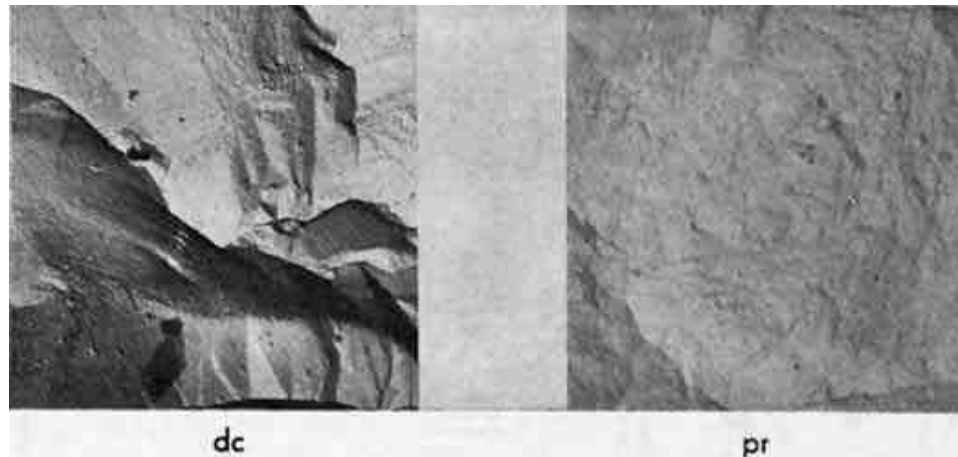


Figure 3 - Fast-cycle pr smooths nickel deposits from a plain Watts bath. Original magnification: 8800 $\times$ .

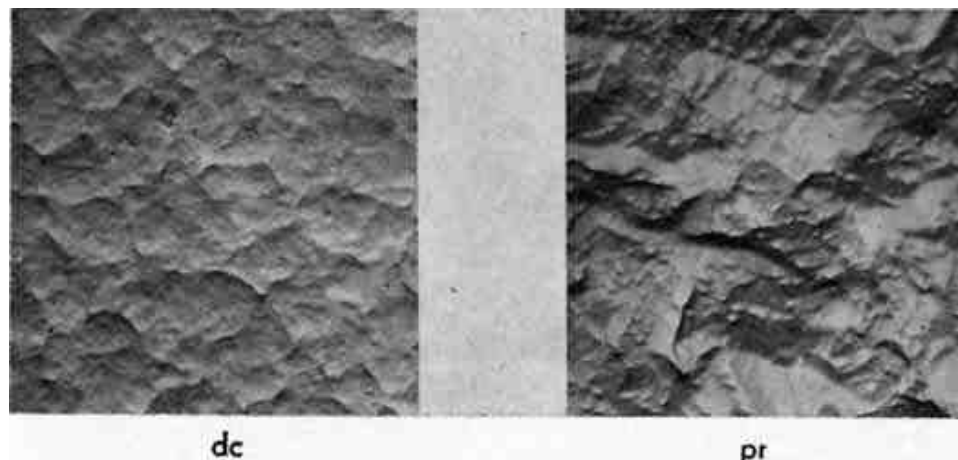


Figure 4 - Fast-cycle pr roughens nickel deposits from a bright-plating Watts bath. Original magnification: 8800 $\times$ .

### Internal structure

Transmission electron diffraction has proved to be a useful technique for the investigation of the atomic structure and other fine-structure characteristics of electrodeposits and other metal-finishing coatings having a very small grain size. This is well illustrated by an investigation of the structure and metallurgical properties of electroless nickel.

Although x-ray diffraction patterns of electroless nickel exhibit the diffuseness that is characteristic of amorphous materials and although for many years it was generally accepted that the deposits were structureless, it was hard to accept this view from a metallurgical viewpoint. Truly amorphous metals are almost unknown, and amorphous alloys are even rarer (and it must always be remembered that electroless nickel is really a nickel-phosphorus alloy). Furthermore, electroless nickel is responsive to heat treatment in a manner that has all of the characteristics of precipitation hardening. Inasmuch as the mechanism for this hardening phenomenon involves conformation of solute atoms to the lattice of the solvent, it is hard to see how an amorphous material (which obviously has no lattice) could be precipitation-hardenable. There are several things that could make the x-ray patterns diffuse other than amorphous structure. The grain size could be exceedingly small or the deposit could contain certain types of lattice defects, such as stacking faults, that tend to make diffraction patterns diffuse.

Electron diffraction, which is generally more troublesome of both execution and interpretation than x-ray diffraction, can be used with much smaller grain size than x-rays and it is not so readily affected by some defect structures. By use of this technique Graham, Lindsay and Read<sup>4</sup> were able to obtain sharp diffraction patterns for electroless nickel of moderate phosphorus content. An example appears in Fig. 5. For higher phosphorus concentrations the patterns are more diffuse, but they still indicate crystallinity rather than amorphicity, as shown in Fig. 6. Additional evidence of crystallinity through use of x-ray diffraction for revelation of preferred orientation (which must involve a lattice) is given in the original publication.<sup>4</sup> Figure 7 is a transmission electron micrograph of electroless nickel. One would hardly expect to see any structure at all in an amorphous deposit.

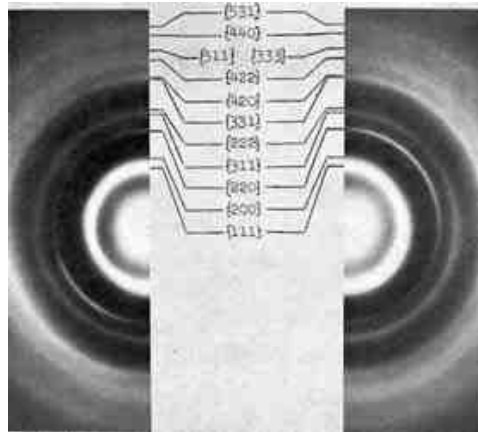


Figure 5 - Electron diffraction pattern obtained by transmission on a thinned as-plated electroless nickel deposit (5% P).

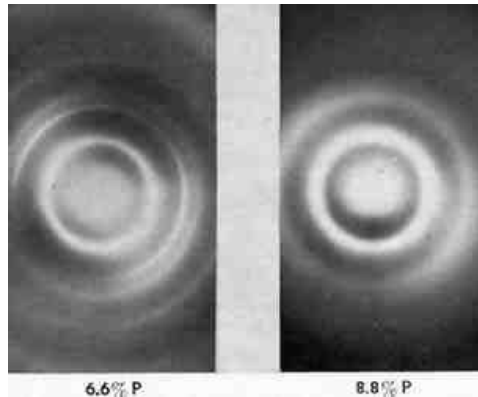


Figure 6 - Increasing phosphorus content decreases the sharpness of the rings in electron diffraction photographs of electroless nickel.

### Mechanical properties

The properties of metals which involve their ability to undergo deformation or to react to the forces that cause deformation are known as mechanical properties. Hardness, strength, ductility, elastic modulus and internal or residual stress are examples. All of these factors contribute to the serviceability of metallic coatings.

Until comparatively recently, the two mechanical properties of electrodeposited metals that have received the most attention and have enjoyed the most popularity are hardness and internal stress. It is not unlikely that the ease with which either property may be measured has had something to do with the popularity. One should hasten to point out, however, that hardness is not really a property at all; rather, it is a combination of properties, all of which depend on the test that is employed. The combination may or may not have some useful relationship to one or more significant properties, such as ductility, tensile strength, or wear

resistance. Internal stresses, on the other hand, have a very real significance as the source of warping in electroforms or of cracking in protective and decorative electrodeposits.

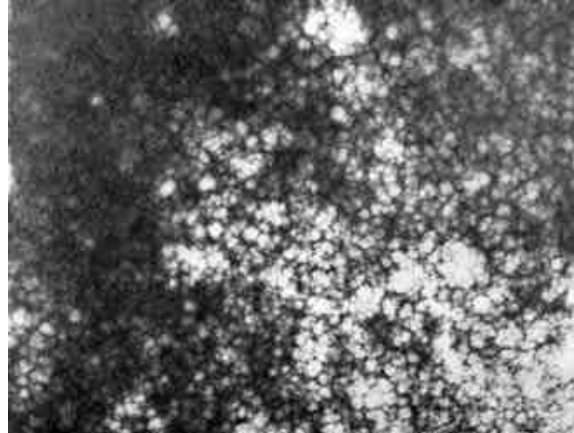


Figure 7 - Transmission electron micrograph of electroless nickel (6.1% P). Original magnification: 124,000 $\times$ .

### *Hardness*

Because of the thinness of most electroplated coatings, it is necessary to use microhardness tests for hardness determinations, and they are subject to considerable subjectivity in the testing procedure. Aside from this, it appears, as will be described in detail later, that hardness determinations bear little consistent or useful relationship to important properties, such as tensile strength or ductility. Because of the relative ease with which hardness measurements can be made, it is important and desirable to use them as control methods insofar as is practical. The important point is that one must establish by experimental methods the relationship that actually exists between hardness and some specific property of concern. No general relationship (such as an inverse relationship between hardness and ductility) can be assumed for electrodeposits. Although in ordinary metallurgical experience certain general relationships can be assumed, there are other exceptions to the rule in addition to electrodeposits. Powder-metallurgy products are examples in point – hardness measurements on them are useless except for control purposes, where some consistent relationship to a significant property has been demonstrated.

Figure 8, adapted from one prepared by Diggin,<sup>5</sup> is a compilation of data from the literature on the hardness of some electrodeposited metals. The solid vertical bar represents the range of values that have been reported for a specific metal. Hardnesses more commonly encountered are shown by the dashed vertical bar. It is rather obvious that there is a great deal of variability in the relationship between the possible range of hardness for a given metal and the range commonly encountered in practice.

### *Internal stress*

Although stress seems from the literature to be a rather easily measured quantity, it appears that there are difficulties in reproducing results from one laboratory to another.<sup>6</sup> In spite of this, it has been possible to establish that some solutions for the deposition of a given metal are consistently more prone to the production of high internal stress than others. The striking differences thus established have tended to obscure the fact that for a given solution the operating conditions may be highly significant. Figure 9 from a paper by Max<sup>7</sup> shows that for three different temperatures of operation the minimum stress is the same and is encountered at about the same current density. The important point, however, is that rarely, if ever, can one attain uniform current density on all parts of a workpiece. In the case in point, therefore, one should choose 60°C (140°F) as the operating temperature so that a considerable range of current density at which uniform internal stress is attained can be utilized. It is probable that variations in internal stress from place to place on a workpiece are just as significant as the absolute value of the stresses.

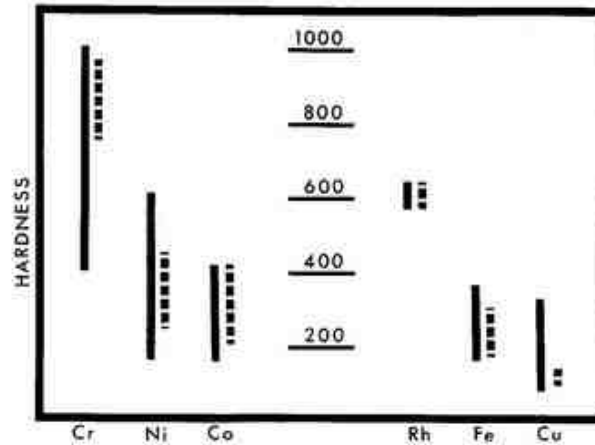


Figure 8 - Hardness ranges for some electrodeposited metals. Solid bars indicate reported extremes. Dashed bars show the range commonly encountered in commercial practice.<sup>5</sup>

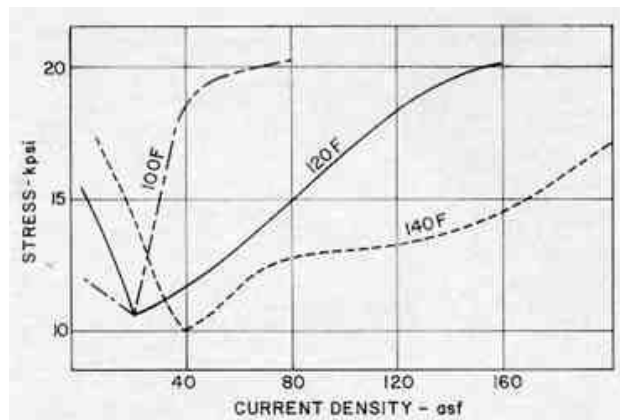


Figure 9 - Relationship between internal stress, current density and bath temperature.<sup>7</sup>

Actually, all of the methods of stress determination commonly employed require a special test specimen and cannot be carried out on an irregularly shaped workpiece. X-ray methods of stress determination would appear to be applicable to local determinations on actual plated objects. Bush and Read,<sup>8</sup> as well as others, have examined some of the problems, both analytical and experimental, that are involved. The results are rather discouraging. In addition to the costly equipment that is involved and the time required for analysis of data, both precision and accuracy are far from what one would like. Under the best conditions, an accuracy of 41.4 MPa (6000 psi) appears to be possible. Although this is not very satisfactory, it does permit one, if he wishes, to determine whether great differences exist from place to place on a workpiece, for the diameter of the X-ray beam with which the measurements are made is only a few thousandths of an inch.

### *Strength and ductility*

Because the ordinary tensile test is not well adapted to the determination of strength and ductility of electrodeposits, Prater and Read<sup>9</sup> adopted the hydraulic bulge test and devised an optical means of measuring the bulge height (to avoid distortion of the thin specimens by the dial indicator ordinarily used). Read and Whalen<sup>10</sup> effected some mechanical improvements in the equipment, and their apparatus is shown in Fig. 10.

Table 1 provides some typical data for electrodeposited nickel. Fracture stress is equivalent to tensile strength. Fracture strain is a measure of ductility, but it is obviously not the "per cent elongation" used by engineers. Rather, it is a truer measure of ductility used by engineering mechanists. It takes into account the change in shape of the specimen as deformation proceeds



during the test. Because it is a logarithmic function, a doubling of the fracture strain means that the ductility is far more than doubled. Prater and Read<sup>9</sup> have discussed the concept of “significant strain” as a measure of ductility and it is this that we use as a measure of fracture strain.

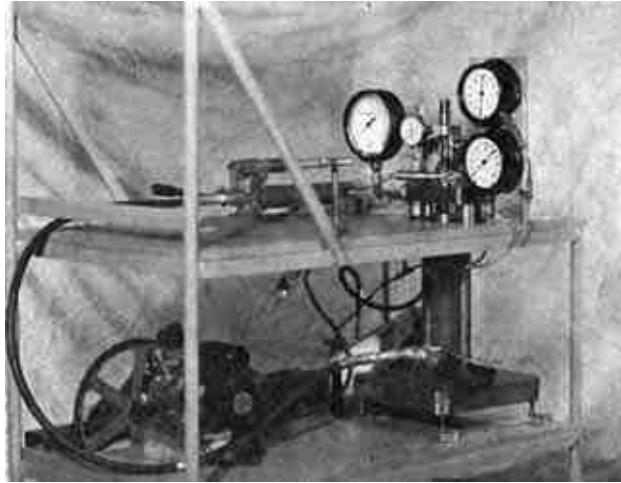


Figure 10 - One version of the hydraulic bulge tester.

Table 1 - Mechanical properties of electrodeposited nickel – about 1 mil thick.

Bath	Fracture stress, MPa (psi)	Fracture strain	Hardness, KHN <sub>25</sub>
Watts (peroxide)	800 (116,000)	0.011	300
Watts (wetting agent)	317 (46,000)	0.011	290
Proprietary A	1270 (184,000)	0.017	660
Proprietary B	1370 (198,000)	0.025	650
Proprietary C	669 (97,000)	0.009	540

The first thing that strikes one on examination of Table 1 is the remarkable range of values for each of the properties. Perhaps this would not be so impressive for an alloy as for a single metal. Then there would be several possible mechanisms for variation of properties, and rather wide ranges might be expected. But for a single metal the variation in strength, for example, in going from one solution to another is astounding.

The second major observation that one makes almost immediately involves the radical departure from the usual interrelationships between properties. Ordinarily, ductility decreases with increasing strength, and hardness varies more or less directly with strength and inversely with ductility. The departures from these generalizations are obvious in Table 1. That nickel is not an exception is shown by the data for copper in Table 2. Although the values for Acid A and Acid B follow the usual relationships, more and more exceptions appear as one examines the remainder of the data. Others have observed similar unusual relationships, particularly the failure of hardness tests to reveal trends in strength and ductility. Some data in point have been reported by Struyk and Carlson,<sup>11</sup> and they are summarized in Table 3. Note that in this instance all deposits were made from the same type of solution. Alterations in plating conditions alone were sufficient to effect marked changes in mechanical properties.

The wide variations in properties caused by changes in solution composition (particularly by addition agents) and operating conditions probably mean that one can never rely on published data, but must be prepared to make mechanical property tests on specimens plated from the actual solution being used under prevailing operating conditions. Fortunately, the hydraulic bulge test is simple, quick and inexpensive, and there is no reason why it cannot be used for routine shop control.

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Table 2 - Mechanical properties of electrodeposited copper - about 1 mil thick.

Bath	Fracture stress, MPa (psi)	Ductility, % Elongation	Hardness, KHN <sub>25</sub>
Acid A	131 (19,000)	1.87	85
Acid B	393 (57,000)	0.60	168
Acid C	262 (38,000)	0.38	188
Cyanide A	296 (43,000)	0.47	161
Cyanide B	296 (43,000)	0.46	200

Table 3 - Mechanical properties of thick fluoborate copper deposits.

Plating conditions	Tensile strength, MPa (psi)	Ductility, % Elongation	Hardness, R-15T
A	224 (32,500)	3.2	69
B	200 (29,000)	14.5	61
C	118 (17,100)	7.3	45
D	200 (29,800)	11.0	67

It has been our experience that ordinarily the basis metal on which a deposit is prepared has little or no effect on the mechanical properties.<sup>10</sup> Unhappily this is not always so, and one must be on the lookout for an exception such as that given in Table 4. The odd thing about these data is that they prevailed for only one lot of copper. Similar treatments to other lots yielded identical results for both strength and ductility. We have encountered one or two other instances of atypical behavior; they are just frequent enough to remind one continually that care should be exercised in selecting basis materials.

Table 4 - Basis metal effects - Watts nickel on copper.

Basis metal condition	Fracture stress, MPa (psi)	Fracture strain
As-rolled	758 (110,500)	0.014
Electropolished	434 (63,000)	0.016

### *Effect of heat treatment on mechanical properties and structure*

Although the heat treatment of electrodeposited metals produces some effects, alloys are much more strikingly affected. Electroless nickel is, of course, an alloy, usually of nickel and phosphorus, and because it is deposited in the form of a metastable solid solution, it responds nicely to heat treatments well below the annealing (or recrystallization) temperature. The following examples of structure and property changes have been selected from a paper by Graham, Lindsay and Read.<sup>4</sup>

Figure 11 shows that the strength of as-plated electroless nickel from an alkaline bath varies markedly with phosphorus content, but this important fact is not revealed by hardness measurements, which are not much affected by the phosphorus concentration in the deposits. The ductility likewise changes a great deal with variations in phosphorus content as shown in Fig. 12, but notice that the strength and ductility both increase with increasing phosphorus content. It is evident that at least some electroless deposits have the same disregard for customary metallurgical relationships that has been found for their electrodeposited brethren!

But the heat treatment of the deposits revealed some surprising behavior. As shown in Figs. 13 and 14, we found, as have others, that 2 hr at 750°C gave a notable increase in hardness with increasing phosphorus content, but there is a catastrophic decrease in strength and ductility for the alloys with 7% or more of phosphorus that hardness measurements do not reveal. The rapid changes in the neighborhood of 7% phosphorus can be explained by examination of the structure of the heat-treated alloys.

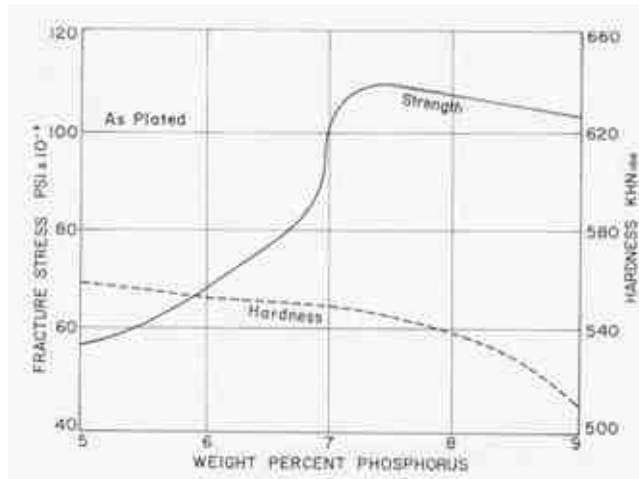


Figure 11 - Effect of phosphorus content on strength and hardness of electroless nickel deposited from an alkaline bath.

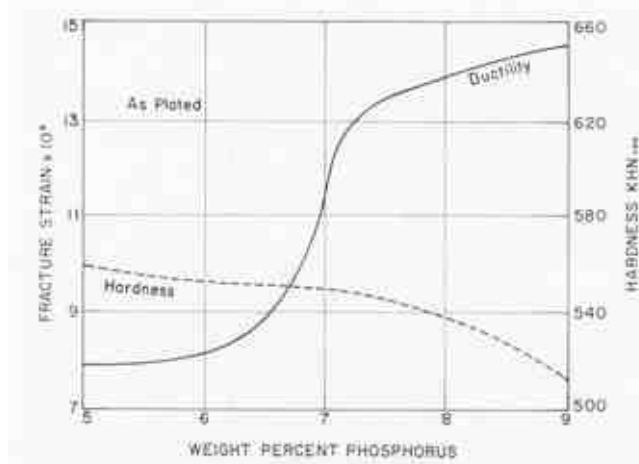


Figure 12 - Effect of phosphorus content on ductility and hardness of electroless nickel deposited from an alkaline bath.

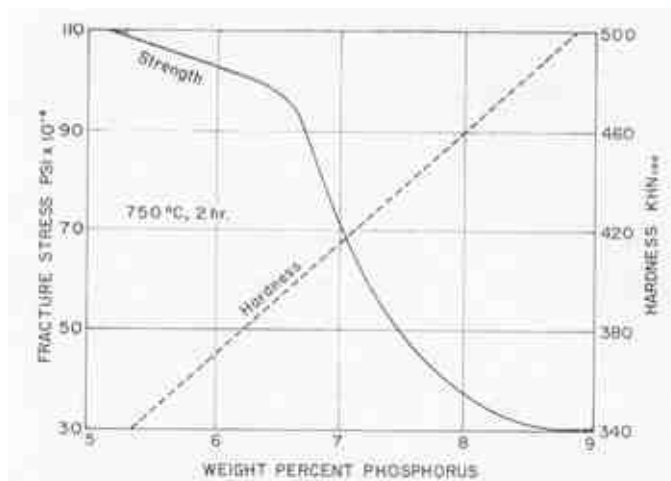


Figure 13 - Effect of phosphorus content on strength and hardness of electroless nickel heated at 750°C for 2 hr.

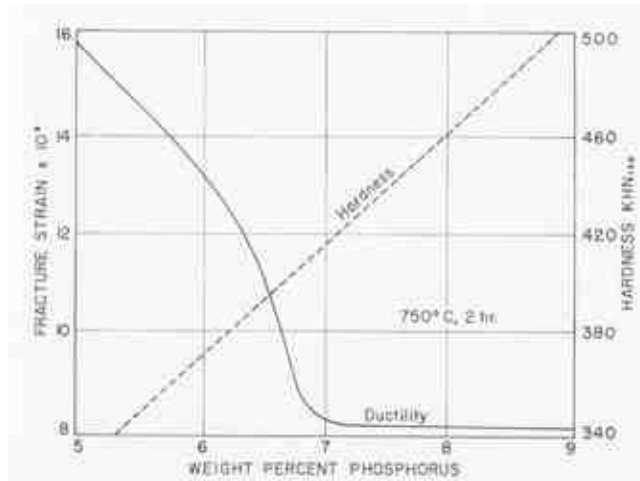


Figure 14 - Effect of phosphorus content on ductility and hardness of electroless nickel heated at 750°C for 2 hr.

Figure 15 contains photomicrographs of three alloys etched to show nickel as light areas and nickel phosphide as dark areas. Below 7%, the continuous phase is nickel. Inasmuch as the continuous phase of a two-phase alloy ordinarily determines its mechanical behavior, the low-phosphorus alloys should be ductile. This is confirmed in Fig. 14. At 7% of phosphorus one cannot determine from the photomicrographs which constituent is the continuous phase; hence, it is not surprising to find a rapid change in ductility.

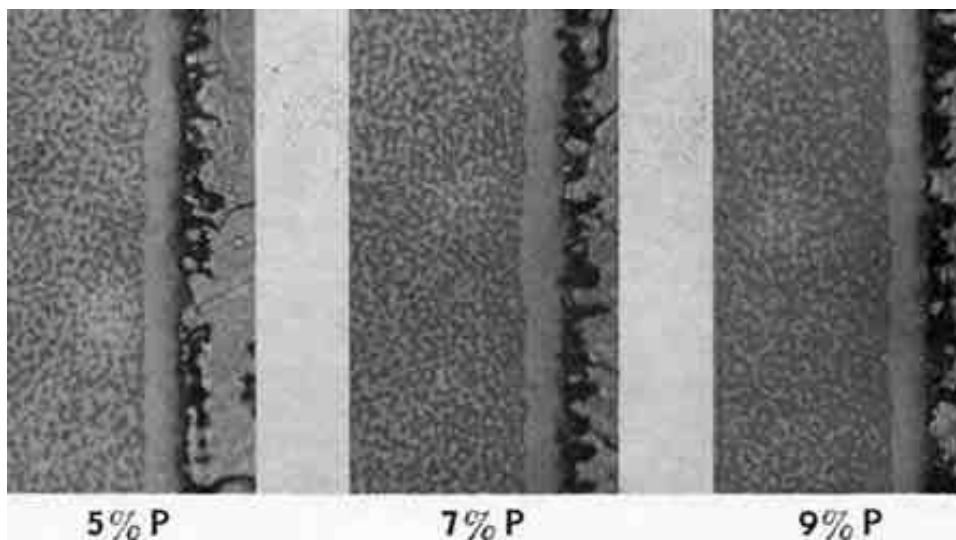


Figure 15 - Photomicrographs of three electroless nickel deposits heated for 2 hr at 750°C. Cyanide-persulfate etch followed by natal. Original magnification: 1,000x.

At 9% phosphorus there is no doubt that the intermetallic compound, nickel phosphide, is the continuous phase. This is an extremely brittle material, and accordingly the ductility becomes very small. The results of chemical etching shown in Fig. 15 were confirmed by the positive chemical identification that is possible by making electron backscatter micrographs such as those shown in Fig. 16. Here the light areas caused by nickel show that nickel is the continuous phase below 7% phosphorus and a phosphorus-rich phase is continuous above this concentration. From the equilibrium diagram for the nickel-phosphorus system, one can deduce that the phase is nickel phosphide.

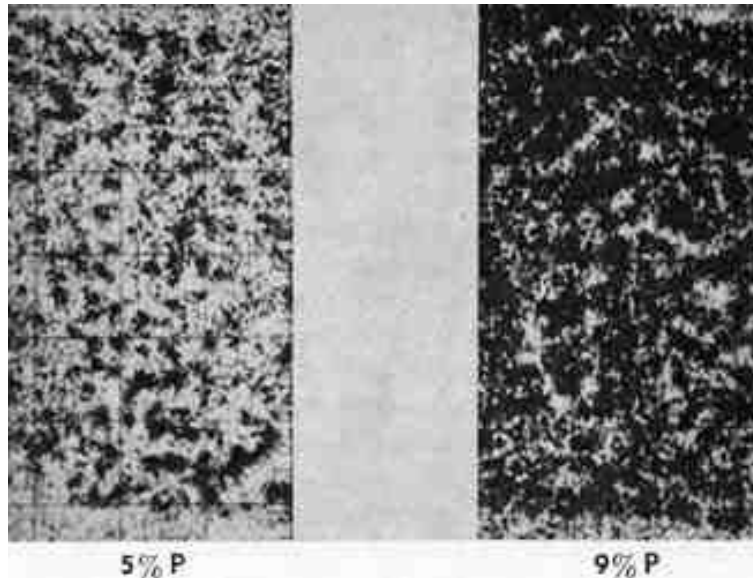


Figure 16 - Electron backscatter micrographs of electroless nickel deposits heated for 2 hr at 750°C. Light areas are nickel-rich. Original magnification: 2,500×.

### *Elastic modulus*

In a variety of calculations relating to problems of internal stress and to differential expansion between basis material and deposit, the elastic modulus of the deposit becomes a factor of considerable significance. Notice that the phrase "basis material" has been used in the preceding sentence rather than "basis metal." The increasing use of electrodeposited metallic coatings on plastic workpieces has focused attention on the differential expansion and contraction effects that are particularly troublesome in the metal-plastic combination, leading as they do to loss of adhesion.

Although some measurements of elastic behavior of electrodeposited metal have been reported, most of the work has been concerned with rather thick, electroformed specimens. Such material is convenient for use in determinations of the elastic modulus by means of conventional tensile testing methods. Read and Graham<sup>12</sup> utilized the sonic method for determination of the modulus of electrodeposited copper a few mils thick, thereby approaching fairly closely the thicknesses used in protective and decorative coatings. The types of solutions and the operating conditions were those that would be used customarily in metal finishing operations.

No significant or interesting variations in the elastic modulus were encountered as a result of varying the operating conditions within the range where a solution could be used to produce acceptable deposits. Table 5 shows, for example, that current density and thickness have little effect on the modulus values for deposits from a single bath. It is another matter, however, when one considers the effect of solution composition, as shown in Table 6. As indicated, the modulus for ordinary copper (in the form of a tube so that it is comparable directly to the tubular electrodeposited specimens) is  $18.1 \times 10^6$  psi compared to  $14.0 \times 10^6$  psi for the plated sample that showed the greatest deviation from the "handbook" value. The  $18.1 \times 10^6$  psi agrees well with the accepted value, indicating that the sonic technique as practiced in the experimental work reported by Read and Graham<sup>12</sup> is satisfactory and that the values found for the electrodeposited samples are real and significant. Because the extreme deviation from the handbook value was 23%, it is evident that in any calculations of the elastic behavior of electrodeposits, one should use modulus values that have been determined experimentally for the exact material under consideration.

Table 5 - Elastic modulus of electrodeposited copper (in million psi).

Current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	Thickness, mil		
	3	6	9
0.54 (5.0)	15.4	15.7	15.7
1.08 (10.0)	15.3	15.9	15.9

Table 6 - Elastic modulus of electrodeposited copper.

Sample	Modulus, MPa (Mpsi)	Deviation, %
Sulfate A	96,500 (14.0)	23
Sulfate B	110,000 (15.9)	12
Cyanide	110,000 (15.9)	12
Drawn tubing*	125,000 (18.1)	---

\*Not electrodeposited. Measurement made for reference and for check of technique

This variation of the elastic modulus of electrodeposited copper can be readily understood by considering the fact that there is a notable anisotropy of elastic properties in a single crystal of copper. If a polycrystalline deposit of copper is composed of grains or crystals that exhibit preferred orientation it is not at all improbable that these grains will be oriented in a direction where the anisotropy is pronounced and the elastic modulus is quite different from the handbook value. In other words, the polycrystalline material will behave to some extent as if it were a single crystal.

It is well known that the kind of plating solution used in depositing a metal has a marked effect on the extent and character of preferred orientation. This is in agreement with the finding that the kind of solution employed was more influential in determining the value of the modulus for copper than the operating conditions.

### Effects of hydrogen charging on the mechanical properties of the electrodeposited nickel

Intrigued by some early work of Phillips and Clifton<sup>13</sup> on the influence of chromium plating on the strength and ductility of nickel deposits, Read, Karchner and Patrician<sup>14</sup> carried out a more comprehensive investigation and found that the effects of chromium plating depended on the bath from which the nickel was plated. In discussions of this work, it was frequently suggested that the effects were caused by hydrogen deposited during the chromium plating operation rather than by the chromium itself. Observations by Read and Baughan<sup>15</sup> indicated that the effects of both hydrogen charging and aging time after charging should be studied apart from the complicating aspects of chromium deposition. Accordingly, Read and Oles<sup>3</sup> used a variety of solutions as well as dc and fast-cycle pr plating to produce deposits having the variety of mechanical properties shown in Table 7.

Table 7 - Mechanical properties of as-plated nickel deposits.

Bath	Current Type	Fracture stress, MPa (psi)	Fracture strain
Watts - Com.	DC	883 (128,000)	0.022
Watts - Higgs	DC	441 (64,000)	0.024
Watts	DC	469 (68,000)	0.033
Watts	PR	469 (68,000)	0.055
Bright A	DC	1590 (230,000)	0.040
Bright A	PR	752 (109,000)	0.036
Bright B	DC	1190 (173,000)	0.039
Bright B	PR	558 (81,000)	0.019

After being charged with hydrogen by cathodic treatment in a cyanide solution, samples were tested at various elapsed times after charging until the embrittling and weakening effects of hydrogen occlusion disappeared (or until the supply of samples was exhausted). The strength and ductility data were plotted on identical elapsed-time coordinates so that recovery times could be compared directly. Four such sets of curves are shown in Figs. 17 thru 19, and it is immediately apparent that there are great differences in the rate of recovery of strength and ductility, depending on how the nickel was deposited; that is, the kind of solution employed. The use of fast cycle pr also had notable effects.

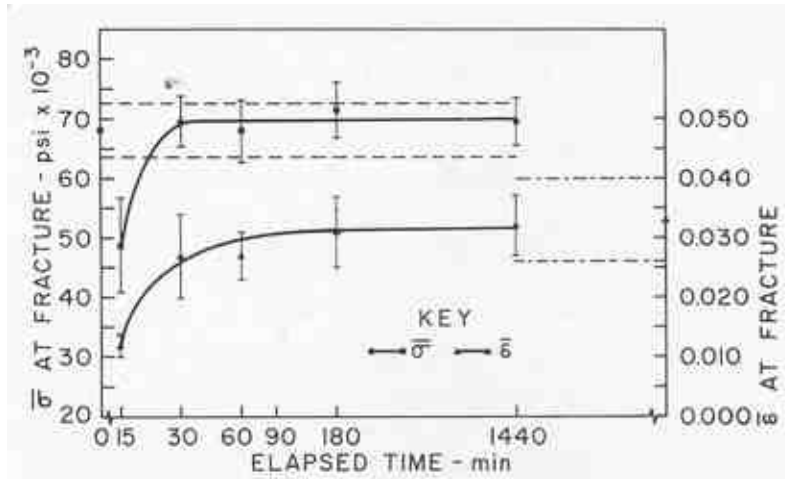


Figure 17 - Changes in strength and ductility of Watts nickel with aging time after hydrogen charging. Standard deviations for as-plated properties shown by dotted lines. Vertical lines at points represent standard deviations for the data.

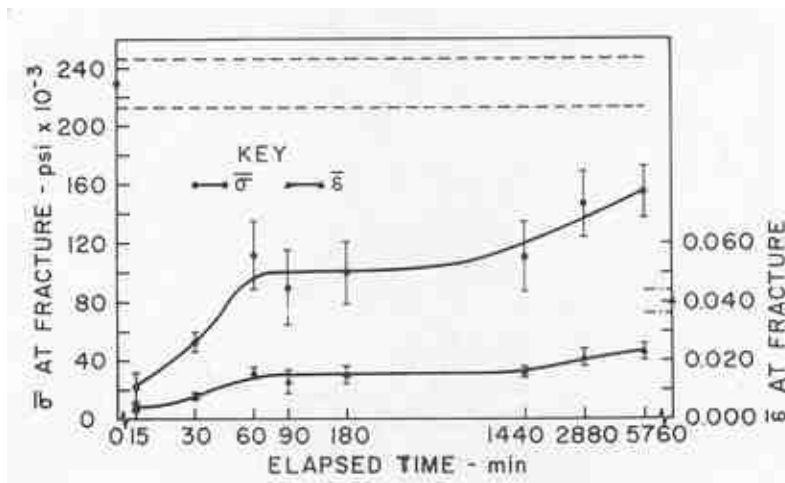


Figure 18 - As in Fig. 17 except for deposits from a bright-nickel bath.

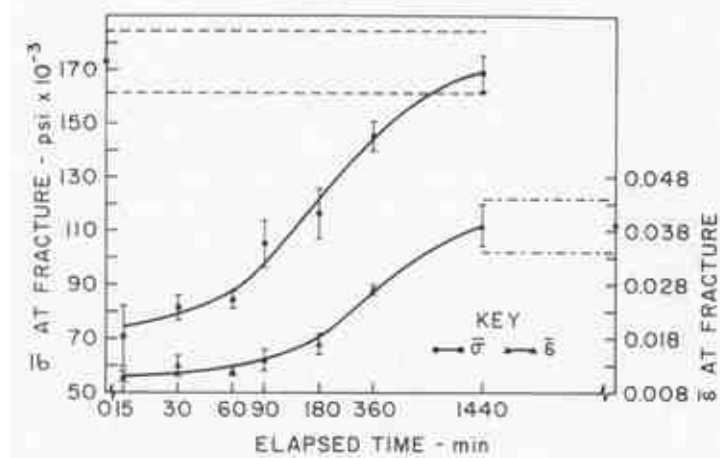


Figure 19 - As in Fig. 17 except for deposits from another bright-nickel bath.

Table 8 is a summary of representative data on the time required for the deposits to recover their original properties after being embrittled and weakened by hydrogen charging. Although no real explanation can be offered presently to account for the differences in behavior, it is perhaps significant to note that so far we have found that samples which show particularly long recovery times have no preferred orientation. Also, it appears from limited observations by transmission electron microscopy at rather high magnifications that samples with numerous dislocation pile-ups at subgrain boundaries, such as those shown in Fig. 20, will lose their hydrogen more rapidly than samples which are relatively free of dislocations. In this connection it is interesting to note that Bastien,<sup>16</sup> working in the general field of hydrogen embrittlement and stress corrosion, has suggested that dislocations are involved in hydrogen movement in metals.

**Table 8** - Recovery time in minutes after hydrogen charging.

Bath	Current Type	Strength	Ductility	Orientation
Watts - Com.	DC	120	180	Preferred
Watts	DC	30	180	Preferred
Watts	PR	360	360	Preferred
Bright A	DC	5800	5800	Random
Bright A	PR	360	360	Preferred
Bright B	DC	1440	1440	Random
Bright B	PR	---*	---*	Preferred

\*Neither weakened nor embrittled.



**Figure 20** - Electron transmission micrograph of thinned, as-plated nickel deposit from Watts bath. Original magnification: 40,000 $\times$ .

### Electrical resistivity measurements in the study of alloy deposits

One of the most metallurgically fascinating aspects of electrodeposits is the variety of structures that can be obtained in alloys - structures that often cannot be produced by any other known method of alloy preparation. These unusual structures are, of course, metastable, and the deposits will be converted on heating to the stable structures and phases that one would expect from the equilibrium diagram for the system involved. In many cases, however, the temperature required to do this is far enough above the atmospheric temperature range to permit practical use of the unusual properties of the as-plated alloy.

The determination of the structure of an alloy involves at one time or another a variety of experimental techniques, although in recent years X-ray and electron diffraction are the most generally useful methods - as indicated by some of the investigations described previously. But one should not neglect the other techniques that metallurgists find useful on occasion. One of these is electrical resistivity, and Read and Shores<sup>17</sup> were able to use it to advantage as one of several tools in studying the structure of



some aluminum-manganese alloys electrodeposited from a fused-salt bath by the method described by Austin, Vucich and Smith.<sup>18</sup>

When the electrical conductivity of an Al-18Mn alloy in the as-plated condition was measured as a function of temperature, the data as shown in Fig. 21 fell on a line with negative slope, that is, the resistance decreased with increasing temperature. This is contrary to the behavior of normal metals and alloys and is characteristic of the class of materials called semiconductors. It was found from a survey of the literature that the intermetallic compound  $MnAl_7$  is a semi-conductor. On the basis of other work, it seemed that the alloy might be a mixture of a supersaturated solid solution of manganese or a manganese compound in aluminum and free particles of the compound  $MnAl_7$  too finely dispersed for certain identification either by microscopy or x-ray diffraction. If the solid solution were highly supersaturated, it would be a very poor electrical conductor, and it would not be impossible that most of the current would be carried by the dispersed compound. Hence, the deposit as a whole would show the negative coefficient that was found experimentally.

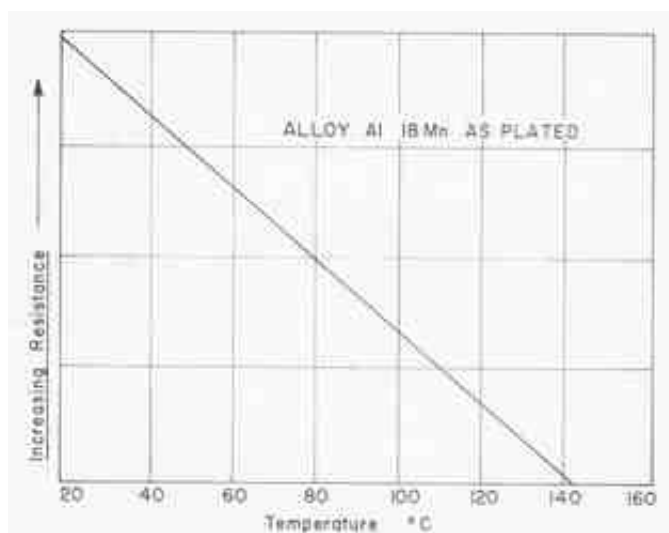


Figure 21 - Temperature-resistance relationship for as-plated aluminum-manganese alloy.

It is now possible, however, to make a prediction on the basis of the hypothetical structure described in the preceding paragraph. If one would cause the solute to precipitate from the supersaturated solid solution, then the predominant phase in the structure should be a very dilute solid solution of manganese in aluminum. Because this is a good, regular metallic conductor, the temperature coefficient of the treated specimen should become positive. Precipitation was effected in a specimen by holding it at 230°C for 19 hr, and as predicted, the slope of the curve became positive as shown in Fig. 22.

This is but one example of the detective work that is required to characterize the structure of electrodeposited alloys - detective work that is often complicated by the unusual, metastable structures that are encountered. This even extends to phases that never appear in equilibrium diagrams.

### A final comment

Perhaps there are those who find the complexity of structures and properties of electrodeposits a discouraging business. I take quite a different view. The range of properties that can be obtained offers the electroplater the possibility of tailoring his deposits to the requirements of the consumer, but he must accept the challenge involved in the control of any complex system.

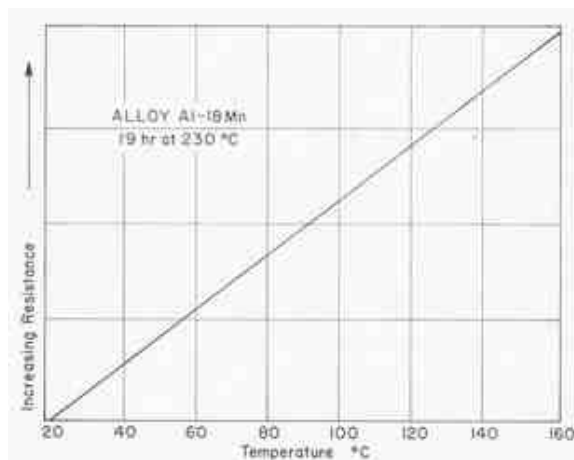


Figure 22 - Temperature-resistance relationship for an aluminum-manganese alloy heat-treated at 230°C for 19 hr.

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**About the author** (from the biography printed in 1964 at the time of his receiving the AES Scientific Achievement Award)



**Dr. Harold James Read** was born in Dubuque, Iowa, on February 14, 1911. He grew up and attended elementary and high schools in various towns in northern Illinois and entered the University of Illinois in the fall of 1928. His undergraduate college career was interrupted twice for a total of two and a half years, working at various jobs ranging from assembling radio switches on a factory assembly line to writing most of a book on Louisiana tax laws. After earning a B.S. in liberal arts and sciences with a major in chemistry in seven semesters in 1934, he entered graduate school at Illinois to major in chemistry and minor in philosophy. His Masters degree was earned in two semesters while working part-time as a chemist and mathematician in the Engineering Experiment Station at the University of Illinois. That was in 1935.



## The William Blum Lectures



### #07 - Harold J. Read - 1966

He accepted an appointment as an assistant instructor at the University of Pennsylvania in the fall of 1939, providing an opportunity to work part time on his doctorate. He taught electrochemistry and quantitative analysis. Chosen as the DuPont Fellow in 1937-38, he received his Ph.D. in February 1939. His thesis on measurement of porosity in metals by gas diffusion was done under Dr. Martin Kilpatrick and portended future interest in metallurgy. After receiving his doctorate, he continued at Pennsylvania with the rank of instructor.

Soon after coming to the University of Pennsylvania, Dr. Read met A. Kenneth Graham and began the friendship and collaboration that brought him into the field of electroplating. Dr. Graham's pioneering work in the metallurgical examination and the evaluation of deposits was particularly fascinating to him, and served as an impetus to lead him eventually into the field that has since occupied his attention. He worked with Dr. Graham at intervals during summers and as a part-time employee during the academic year, and they published several papers as collaborators.

Not all of the activities of Drs. Graham and Read were scientific or technical. Dr. Graham's sister-in-law participated in some of the parties at his home, and it was not too long before Catherine Price Braungard became Mrs. Read. Married in 1938, they celebrated their 25th wedding anniversary a couple of years ago by attending together an ASTM Committee B-8 meeting in Chicago. The Scientific Achievement Award recipient is still surprised that she puts up with him, but points out that he at least took her along with him. Although no longer active as a professional, Mrs. Read was employed for several years as a bacteriologist and chemist by a sugar company, and the two Reads collaborated on one publication and she contributed important analytical work to some of his other early publications.

He left the University of Pennsylvania in 1940 to become an Industrial Fellow at Mellon Institute where his assignment was development work for the H.H. Robertson Company of Pittsburgh. With the onset of World War II the character of his work at Mellon Institute changed gradually from chemistry to metallurgy. Furthermore, his next-door neighbor in the Squirrel Hill section of Pittsburgh, Dr. Maxwell Gensamer, then Professor of Metallurgy at Carnegie Tech., inveigled him into some part-time work on the Manhattan Project. This was the straw that tipped the balance. When, shortly after a certain "big bang" in New Mexico, Dr. Gensamer accepted a new position at Penn State, he invited Dr. Read to accompany him as Associate Professor of Metallurgy - officially, that is. Dr. Gensamer always maintained that he needed one screwball metallurgist on his staff and that the best way to get one was to capture a backsliding chemist. Be that as it may, Dr. Read was made Professor of Physical Metallurgy in 1951; his title later being changed to Professor of Metallurgy - the position he now holds.

He has always enjoyed working with his hands for relaxation-in a yard and garden in summer and a basement workshop in winter. During World War II, he taught Mrs. Read to operate several machine tools and the basement workshop became a small factory for machining special test specimens and for constructing microtesting equipment. This activity was continued for a time after the war, but was stopped when he became a full professor.

His basement is still full of machinery and he finds great relaxation in constructing models, building more machinery, and lately, in lapidary work. Occasionally he is seized with a do-it-yourself fever and will rip a room of his house down to the bare studding and joists and then rebuild it in some way different than any other room in his house. There is some question as to who is going to wear out first - Dr. Read or the house (they happen to be about the same age!).

He and Mrs. Read enjoy traveling, particularly in Florida, where they like to fish and boat, and in the National Parks where color photography is a prime activity. When World War II interfered with ordinary travel for pleasure both of the Reads found flying a fascinating outdoor activity and both obtained pilot's licenses in single-engine craft. Although learning to fly was fun, they now prefer their fire-engine-red station wagon filled with fishing equipment, bowling balls and hiking boots and often surmounted by a car-top boat.

His early publications in electroplating and electrodeposition involved polarization studies and the investigation of electrolyte films at both anode and cathode surfaces. But as his work turned to metallurgy, more and more attention was devoted to properties of the deposits rather than to the phenomena prevailing in the electrolyte. His adaptation of the hydraulic bulge test to electrodeposits provided a simple means of evaluating tensile strength and ductility. The availability to him of equipment for electron microscopy, electron diffraction and lately, electron proboscropy, has led to many publications in the field of structure of electrodeposits. Overall, his work in these fields has shown that electrodeposited metals often have unusual structures and properties compared to those prepared by ordinary metallurgical methods.



## The William Blum Lectures

#07 - Harold J. Read - 1966



In 1971 he became a Professor Emeritus of the Pennsylvania State University as he began retirement, although it is clear from the previous text that the word "retirement" was anything but for Dr. Read and his wife. In the ensuing years, they traveled all over the world, touching every continent except Antarctica. Dr. Read passed away on April 19, 1999 in Grove City, Florida.

Throughout his career, Dr. Read developed the underlying principles of metallurgical science and applied them to the unique structure-property relationships of electrodeposits. In the process, he contributed a coterie of scientist and engineers in our industry through his dedicated mentoring of many Graduate students. This paper is a definitive summary of his work.