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A DUAL CELL PLATING APPARATUS FOR DEPOSITION OF MULTI-LAYER METAL SYSTEMS

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BY

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A DUAL CELL PLATING APPARATUS FOR DEPOSITION OF MULTI-LAYER METAL SYSTEMS

Abstract

An experimental dual cell apparatus for the electrodeposition of alternating metal layers (binary systems) employing a rotating cathode is described.

Microstructures of multi-layered systems of Ni-Cu and Ni-Fe are shown and some of their properties are discussed and evaluated. X-ray diffraction data on the behavior of the Ni-Cu systems is given. Also shown is the multi-layered Ni-Cr microstructure.

Data compiled has shown that:
lamellar structures exhibit increasing hardness and smoothness with decreasing thickness of single constituent layers (approximate layer thickness range 23,000 to 60 angstroms); fine grained and fairly pure multi-layered structures are rapidly produced; bulk multi-layered structures of Ni-Cu consisting of uniform and extremely thin layers, exhibited some interdiffusion (as plated), as evidenced by x-ray diffraction patterns; x-ray diffraction data also shows complete interdiffusion of Ni-Cu multi-layers when treated at relatively low temperature and time.

Cross-Reference Data

Chemical

Electrochemistry

Plating

Vapor Plating

DO NOT REMOVE THIS ABSTRACT FROM THE REPORT

CONCLUSIONS

Data obtained from multi-layered structures produced with the dual cell apparatus offer the following conclusions:

a. Bulk multi-layered metal structures (binary systems of Ni-Cu and Ni-Fe) consisting of single layer thicknesses as small as approximately 30A°(i.e. in the case of Fe) may be rapidly produced.

b. Multi-layers of Ni-Cu and Ni-Fe generally exhibit increasing hardness and brightness with decreasing thickness of the single constituent layers within certain limits.

c. Multi-layered structures with single layer thicknesses less than approximately 100A° that have been produced with the plating conditions reported, appear to be too brittle for service use without first subjecting them to thermal treatment.

d. X-ray diffraction patterns indicate some interdiffusion of as-plated thin layers (100 to 50A°) in the Ni-Cu multi-layered system.

e. Complete interdiffusion (solid state) of multi-layers, as evidenced by x-ray diffraction patterns of the Ni-Cu system, may be obtained at relatively low temperatures and time.

This evaluation on the properties of multi-layered structures of thin films produced with the dual cell device is far from complete. It is recommended that studies be continued for developing useful alloys and determining their mechanical properties at increasing cathode speeds.

The application of the dual cell device, both as a research and production tool, should open the doors to many areas of study for both the plater and the metallurgist.

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GLOSSARY

Symbol - A°	Angstrom or Angstrom Unit - a minute unit of length equal to one ten-thousandth of a micron or one hundred millionth of a centimeter, used in expressing the length of light waves.
Anisotropy	A state whereby different properties are exhibited when tested along axes in different directions. Not isotropic.
Cathode C.D.	Cathode current density.
Expitaxial Growth	Arrangement of deposited atoms on a substrate. Growth comes about as a result of an atomic interaction between the substrate and the deposit which under suitable conditions, can exert a directive influence on the nature and orientation of the deposit.
F.C.C.	Face centered cubic
Knoop or Knoop hardness numbers	The Knoop hardness test is applicable to extremely thin metal, plated surfaces, exceptionally hard and brittle materials, very shallow carburized or nitrided surfaces, or whenever the applied load must be kept below 3600 grams. The Knoop indentor is a diamond ground to an enlongated pyramidal form and it produces an indentation having long and short diagonals with a ratio of 7 to 1. The longitudinal angle of the indentor is 172 degrees thirty minutes and the transverse angle 130 degrees. The Tukon tester in which the Knoop indentor is used is fully automatic under electronic control. The Knoop hardness number equals loads in kilograms divided by the projected area of indentation in square millimeters. The indentation number corresponding to the long diagonal, and for a given load may be determined from a table computed for a theoretically perfect indentor. The load, which may be varied from 25 to 3600 grams, is applied for a definite period, and always normal to the surface tested. Lapped plane surfaces free from scratches are required.
R.M.S.	root mean square
R.P.M.	revolutions per minute

INTRODUCTION

In spite of the notable achievements reported in the field of electrodeposition in the past years, the search still continues for improved coatings to meet the increasing demands for higher performance of new materials.

With advances in modern technology many applications with thermal, mechanical and chemical environments cannot be sustained with existing commercial coatings. It has been problems of this nature which has provided the impetus to direct attention towards the development of the dual cell apparatus which may produce coatings and electroformed structures for satisfying prime mechanical, corrosive and high temperature requirements.

BACKGROUND

Composite structures of metal layers has been the subject of intensive study in recent years with many objectives. Such structures range from thin films to bulk deposits of a number of layers and metal combinations. These composite coatings have been deposited by electroplating, spraying, vapor plating, evaporation and also sputtering techniques. Some of the objectives and findings reported by investigators are as follows:

a. Investigations with alternate or duplex electrodeposited coatings [1, 2, 3] of Cr and Ni have demonstrated remarkable improvement in the outdoor protection of ferrous components as compared to the usual composites of Cu-Ni-Cr.

b. Blanchard[4] conducted studies on the oxidation resistance of Mo at elevated temperatures using sprayed, electrodeposited and molten dipped composite metal systems such as Al-Cr-Si. Such a combination showed good resistance to thermal shock.

c. Safranek and Schaer[5] conducted studies with alternate multilayers of Ni and Cr by electrodeposition and subsequent alloying by diffusion for oxidation resistance of Mo at elevated temperatures.

d. Belser[6] investigated aging and alloying of bimetal films produced by plating, evaporation and sputtering techniques on quartz piezoelectric resonators.

e. Sherwood and Himes[7] cite the concept development of multi-layer solid state circuits. Such studies involved the development of thin-films by vapor deposition and pointed out the influence of the substrate on the deposit (i.e. epitaxial growth).

f. Abbott[8] offers a valuable annotated bibliography on "Epitaxial Growth" in thin film technology.

g. Fujiki,[9] through his study on alloy formation by successive deposition of constituent metal vapours in vacuum, found that some metal pairs alloyed and some did not when successively deposited. He attributed this alloying to a temperature rise which was mainly due to the latent heat of condensation of the secondary metal vapour deposited on the substrate layer. The structural defects in the substrate layer also seemed to contribute to alloy formation.

The attention given to the investigation of properties of composite coatings as reported in the literature, has largely contributed to the interest given this study.

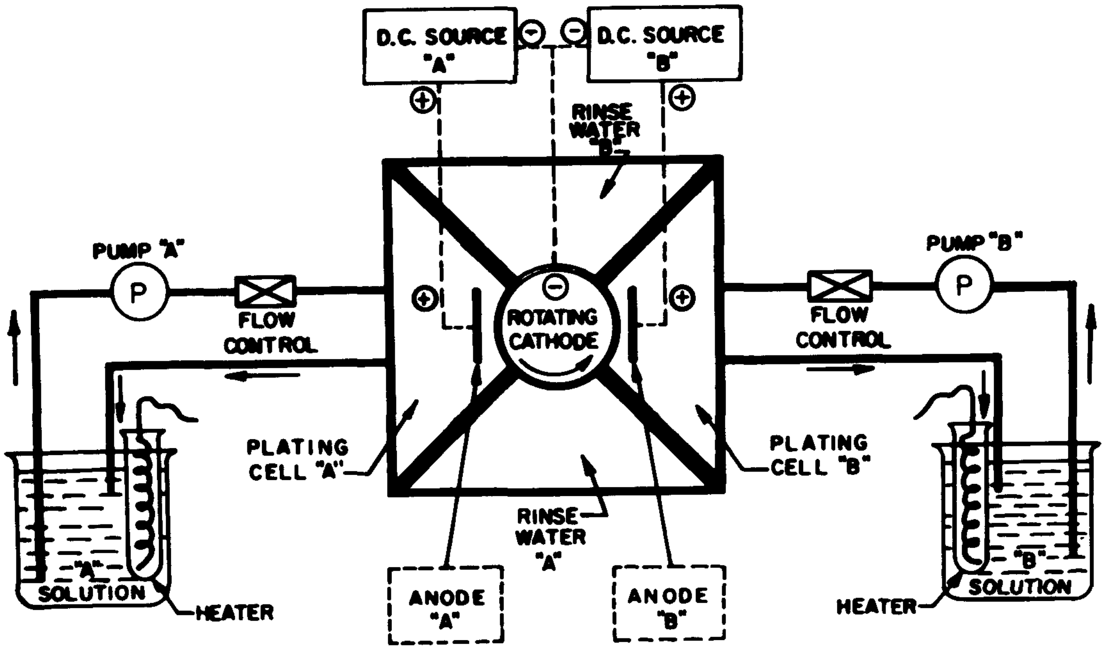
OBJECTIVE

In view of the interesting properties and alloying behavior of thin metal films, an economical method was desired for developing multi-films which could be built up into massive structures which might fulfill future material requirements. Therefore, an investigation was undertaken resulting in the development of a unique and rapid electrolytic process for producing alternate layers of binary, ternary and more complex metal systems with a large range of single layer thicknesses. These multi-layered structures are produced by a multi-cell electroplating device employing a rotating cathode (of a suitable geometrical construction) exposed to the active cells. The cells with which the layers are obtained are isolated from each other. In this manner alternating chemical or electrochemical deposits of lamellar construction, in any desirable proportions and any conceivable thickness of single constituent lamina or layer, may be accomplished.

This report describes the operation and flexibility of a dual cell apparatus and presents some of the data compiled from the multi-layered structures which have been produced with such an apparatus. Such data clearly exemplify the feasibility of obtaining a variety of lamellar and subsequent alloyed structures with the aid of a dual or multi-cell device.

DUAL CELL DEVICE

Since this study has been limited to a dual cell (electrochemical) device, discussion will primarily refer to binary systems. A diagram of a dual cell electroplating apparatus for continuous deposition of binary metal systems is shown in Figure 1. The diagram shows the top view of a four (4) cavity box with two (2) cavities being utilized for the active cells and two (2) cavities for water rinsing. This system shows that multi-layered structures may be rapidly and uniformly deposited in a somewhat interrupted



SCHEMATIC OF A DUAL CELL ELECTROPLATING APPARATUS FOR MULTI-LAYERS OF BINARY METAL SYSTEMS

FIGURE 1

fashion. Two (2) metals are deposited on opposite sides of the rotating cathode at the same time. The thickness of the individual constituent layers are independent of total time and solely dependent on the speed of the cathode for a given set of plating conditions. The seal, which encases the cathode and isolates one cavity from another, may be any suitable material, such as rubber or plastic, that will tolerate the plating environment and also prevent the loss of electrolyte while the cathode is rotating. The cathode for this study was a nickel plated steel rod (3/4 inch diameter and 2 inches long) with a mandrel at the bottom and for connection to a drive motor and a mandrel at the top for the negative contact through the use of a simple alligator clip. The portion of the cathode surface exposed to the active cells is varied by the construction of the cells. The anode to cathode distance for this study was approximately 1.5 inches. The plating solutions are circulated to and from their respective cells in a manner that insures rapid and complete exchange of solution near the cathode surface.

To insure rapid and satisfactory cleaning of the cathode surface, warm running tap water flows at a moderately high rate from the top to the bottom along the cathode surface during its rotation.

The layers are actually deposited on the rotating cathode in a wound or spiral fashion as depicted in the figure below.

SKETCH SHOWING MULTI-LAYERED BINARY
SYSTEM IN A SPIRAL FASHION

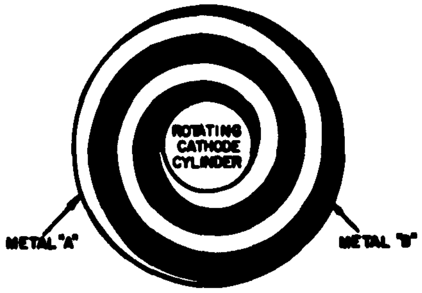


FIGURE 2

Cathode speeds employed for this investigation range from .33 rpm to 92 rpm. However, multi-layered structures have been produced with cathode speeds as high as 1700 rpm which corresponds to a plating time of 4.3 milliseconds. Although test specimens for this study are approximately .006 inches thick, structures measuring approximately .020 inches thick have been produced. Massive structures may be easily obtained by the use of a more flexible cathode seal or by transferring the cathode to another dual cell box in stages as the diameter increases.

An exclusive feature of the device is that the layers may be easily observed in the rinsing cells as deposition takes place on the rotating cathode.

The quality of the multi-layered structures, as in any plating process, will depend primarily on the control of the process variables for a chosen plating bath and upon the selection and combination of the metals in the system.

Plating Conditions

The following baths and plating conditions were used for all specimens:

Copper Bath	Cupric Sulfate, $CuSO_4 \cdot 5H_2O$	28 oz/gal
	Sulfuric Acid, H_2SO_4	7 oz/gal
	Temperature	120°F
	Cathode, C.D.	1 amp/in^2
	Anode	Electrolytic Copper
Nickel Bath	Sulphamate Nickel*	
	Boric Acid, H_3BO_3	5.50 oz/gal
	Temperature	140°F
	Cathode, C.D.	2 amps/in^2
	pH	3.5-5
	Baumé	29.5(@70°F)
	Anode	Electrolytic Nickel
Iron Bath	Ferrous Sulfate, $FeSO_4{-}7H_2O$	32 oz/gal
	Sulfuric Acid, H_2SO_4	adjusted to pH
	Temperature	120°F
	Cathode, C.D.	.7 amps/in^2
	pH	2.8-3.5
	Anode	Electrolytic Iron
Chromium Bath	Chromic Anhydride, CrO_3	33 oz/gal
	Sulfuric Acid, H_2SO_4	.33 oz/gal
	Cathode, C.D.	2 amps/in^2
	Temperature	130°F
	Anode	Lead Sheet

*Barrett Sulfamate Solution type SN

Average coatings for this study are approximately .006 inches in overall thickness.

Conditions for Evaluation of Multi-layers

a. Chemical Analysis - Specimens for analyses were prepared by separating the combined layers from the cathode cylinders in strip form, insuring that no adherence of the substrate took place. Final analyses of both the specimens and solutions indicated approximately 1% or less of impurities by weight. Chemical analysis has shown the Ni-Cu structure to have approximately 60% Ni and 40% Cu by weight. The Ni-Fe structures have approximately 80% Ni and 20% Fe by weight. These percentages compared reasonably close with our calculations for the rates of deposit.

b. Hardnesses - All readings were taken parallel to the cross-sectioned layers and in several areas of the specimen. However, the readings reported here are an average of the readings taken in the center of the structures.

For a comparison, some readings were taken normal to the cross-sectioned layers with no appreciable differences found.

c. Metallography - The photomicrographs shown represent the results of an intensive effort in attempting to reveal the definite grain and interfacial boundaries of the lamellar and alloyed microstructures examined. Some of the multi-layered structures with the thinner constituent layers exhibited profound changes in their chemical resistance when treated with various etchants. Alloying of the structures sometimes resulted in a reverse of chemical resistance. Such changes in the chemical resistance coupled with the relinquishing resolution as the single constituent layers became thinner, were the primary difficulties in the preparation of specimens for 1000 magnification.

Since the multi-layers consisted of relatively thin layers, all microstructures were examined at 1000 magnification. Etchants and etching times in most cases are shown since deviations existed from one specimen to another.

d. Surface Finish - The steel cathodes which were nickel plated (approximately 5 minutes) prior to the deposition of the multi-layers, showed a surface finish of 6-8 RMS. In reference to the surface of the multi-layers, very slow cathode speeds sometimes favored a rough finish due to noduling primarily of nickel. Fast cathode speeds almost always favored smooth and in many cases bright deposits. This seems reasonable in view of the increased wiping action of the cathode seals preventing formation of sites favorable for gas bubbles to cling to the cathode surface during high speeds.

e. X-ray Diffraction - The curved as-plated specimens were held flat by placing them between two (2) glass slides. This was necessary for evaluation with the x-ray diffractometer. The difficulties encountered through this practice were the induced strain of the specimen from bending and the displacement of the specimen, when mounted on the reference circle of the x-ray diffractometer unit, due to the interference of the glass slide. Both of these factors undoubtedly contribute markedly to the shifting of the reference angle resulting in uncertainty for the accurate measurement of lattice parameters. Any heating of the specimens for purposes of annealing, in view of the thin layers, would promote appreciable diffusion, subsequently altering the as-plated structures. Heating was therefore avoided.

The x-ray diffraction peaks given here are intended to show the relationship of the Ni intensity curve with that of the Cu for that same specimen. Comparison of the peaks of curves of one specimen with the other cannot be made, since the frequencies for recording these curves may differ and have not been corrected due to the complications in size.

The primary aim in the data is to show the alloying behavior and determine the phases which exist in the specimens examined. With this information, multi-layered structures of very thin layers are better understood.

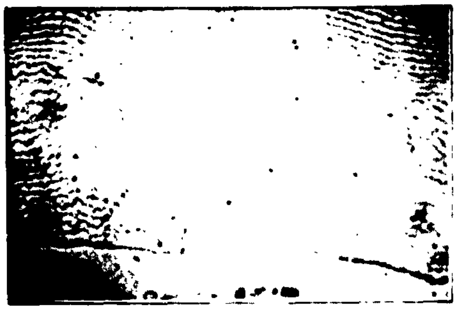
f. Tensile Tests - In view of the greater anisotropy of electro-deposited metals and most especially in this case of multi-layered structures, data on tensile strength, yield strength and ductility would be invaluable. It is well recognized that hardness data alone is insufficient to completely evaluate such multi-layered structures and therefore the necessary steps should be taken to investigate further their mechanical properties. The preparation of specimens from cylindrical cathodes was considered impractical for such tests since the curvatures of the specimens posed problems which would affect the accuracy of the data. Another dual cell device has been developed for producing flat specimens which should satisfy the requirements for mechanical testing; however, further improvement is required for refinement of the new design.

Various Multi-layered Structures

Figure 3 gives a general view of some of the different multi-layered structures which have been produced with the dual cell device.

Since these photomicrographs represent specimens of general interest only and are not part of the group of specimens which have been more extensively examined for this study, only the following brief statements in reference to the structures will be given here:

Figure 3. a. Shows multi-layers of Cu and Ni which are barely resolvable. Close examination of the layers reveals a rippled pattern produced by a non-uniform rotation of the cathode.



Nital Etch (a) 1000X

Ni-Cu STRUCTURE

DARK Cu LAYERS (APPROX. 4000 Å)
WHITE Ni LAYERS (APPROX. 8000 Å)
NOTE: RIPPLED EFFECT IN LAYERS DUE TO NON-UNIFORM CATHODE ROTATION.

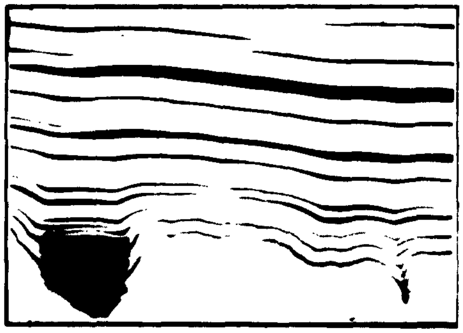
Nital Etch (b) 1000X

Ni-Fe STRUCTURE

DARK Fe LAYERS 7000 Å
WHITE Ni LAYERS 11,000 Å

SAME SPECIMEN

Nital Etch (c) 250X



Nital Etch (d) 1000X

Ni-Fe STRUCTURE

LAYERS TOO THIN FOR RESOLUTION

HCL Etch (e) 1000X

Ni-Cr STRUCTURE

ANALYSIS:-90% Ni; 6% Cr; 4% Unknown

CROSS SECTIONS OF TYPICAL
MULTI-LAYERED STRUCTURES

FIGURE 3

b. Shows a Ni-Fe system with very clear etched layers of Fe. Note the effects of the substrate on the formation of the first few layers.

c. Depicts a different view of Ni-Fe layers taken from the same specimen as b. This offers a good illustration of the layers as they appear at 250 magnification. The micro-pit was apparently caused by a trapped gas bubble.

d. The very thin alternate layers of Ni and Fe are indistinguishable here. Repeated efforts with various etchings to contrast the iron layers resulted in this photomicrograph as the best illustration for examination. This view again shows a number of interesting initial layers following the contour of the substrate.

e. This view is a Ni-Cr system resembling what may be termed a mosaic-like structure. This structure, with a composition of 90% Ni and 6% Cr with 4% unknown, showed a hardness reading above that for hard chromium. However, difficulties with proper rinsing of the Cr solution from the cathode, prevented duplication and confirmation of such specimens. The main problem was the development of structures with sufficient overall thickness for satisfactory hardness measurements.

Examination of Ni-Cu and Ni-Fe Multi-layers

In order to have a more thorough understanding of the influence of one layer of deposit upon another when deposited on a rotating cathode of the dual cell device, the following were examined:

a. The microstructure and hardness of conventional Cu plated on a stationary cathode in one cell of the dual cell box.

b. The microstructure and hardness of alternate layers of Cu plated on Cu on a rotating cathode for various speeds. The Cu-Cu structure was accomplished by using both cells for Cu with the electrolyte circulated from the same reservoir.

c. The microstructure and hardness of Ni plated under the same conditions as a. and b.

d. Finally, the microstructure and hardness of binary systems of alternate layers of Cu and Ni produced with different cathode speeds.

A correlation of cathode speed with single layer thickness and exposure time in the plating cell is given in Table I below, as a convenient cross-reference. Since the multi-layers are not always distinct in the ensuing photomicrographs due to either resolution difficulties or to alloying tendencies, reference will, in the majority of cases, be made to cathode speeds rather than to expected layer thickness. Although single layer thicknesses may vary from one specimen to another the calculations offer a good approximation.

TABLE I

CORRELATION OF CATHODE SPEED, PLATE TIME AND CALCULATED LAYER THICKNESS FOR MULTI-LAYERS

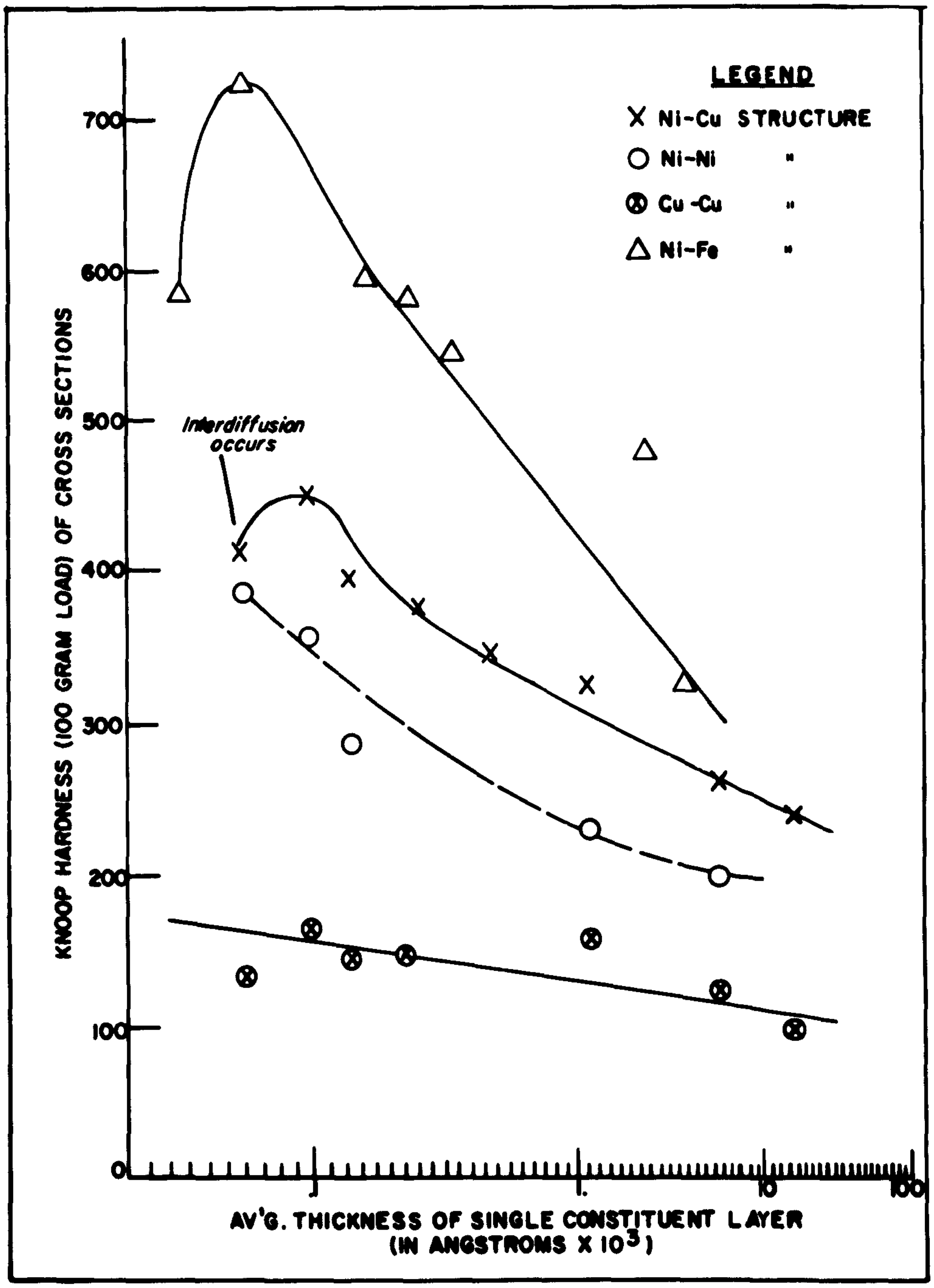
Cathode Speed (RPM)	Plate Time (Sec.) in one cell	Single Layer Thickness in (A°)			Combined Layer Thickness in (A°)	
		Ni	Cu	Fe	Ni-Cu	Ni-Fe
0.33	22.5	22,900	15,250	7,625	38,200	30,525
0.86	8.69	8,100	5,400	2,700	13,500	10,800
4.61	1.62	1,725	1,150	5,075	2,865	6,800
9.00	0.831	722	478	239	1,200	961
16.00	0.467	457	305	152.5	762	610
33.00	0.227	250	154	77	384	327
64.00	0.117	119	79	39.5	198	159
92.00	0.0815	95.5	63.5	31.2	159	126.7

The characteristic hardnesses for the multi-layered structures of Cu-Cu, Ni-Ni, and Ni-Cu that were examined are plotted in Figure 4.

Although the Ni-Fe system has not been as extensively investigated as the Ni-Cu system, the hardness curve for Ni-Fe multi-layers have also been included in Figure 4 and the calculated layer thicknesses have been incorporated in Table I.

It will be noted that the hardnesses are plotted as a function of average thickness of single constituent layers. This seemed to be the simplest method of plotting since all of the systems (i.e. Ni-Ni, Cu-Cu, Ni-Cu and Ni-Fe) were being compared. The average thickness of a single constituent layer for a Ni-Cu structure produced at a cathode speed of .33 rpm is therefore:

$$\text{Average Thickness Layer } (A^\circ) = \frac{\text{Ni-Cu layer combined } (A^\circ)}{2}$$



HARDNESS vs SINGLE LAYER THICKNESS FOR MULTI-LAYERED STRUCTURES OF Cu-Cu; Ni-Ni, Ni-Cu, & Ni-Fe

FIGURE 4

It may be generally concluded in studying the curves (which represents the best data available) that such structures have a tendency to increase in hardness with decreasing thickness of single layers. However, in the case of binary systems, the hardness increases up to a limiting cathode speed (i.e. a minimum layer thickness) and then drops off sharply. A discussion on the chief factor which appears to govern this pattern is merited since this governing factor is recognized by correlating the hardness with the microstructures and x-ray patterns of the test specimens.

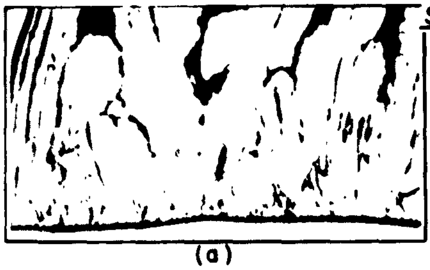
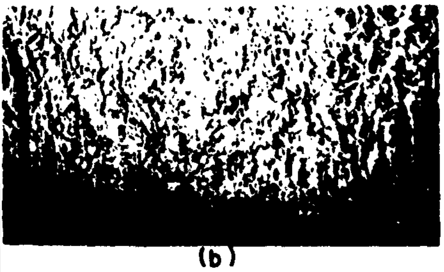
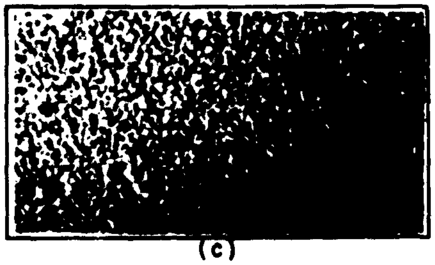
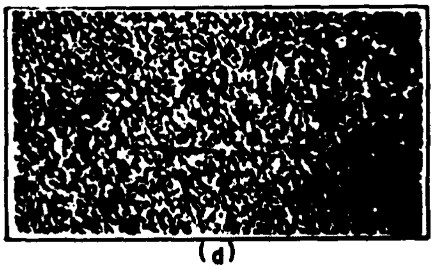
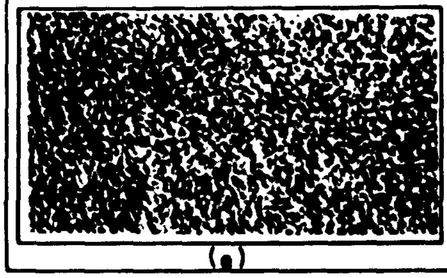
Cu-Cu Structure

The microstructure and hardness of Cu plated with the conditions given (i.e. a conventional deposit) is shown in figure 5. The typical columnar structure of low hardness (57 Knoop) is clearly shown.

The microstructures and hardnesses of successive layers of Cu on Cu plated with various cathode speeds under the conditions given in (b) are shown in figure 5b, 5c, 5d, and 5e. A profound change in microstructure and increase in hardness is noted. A transition from columnar or outward growth to a lateral and fine grain structure takes place. Another characteristic which is noted is that the successive layers of Cu in the homogeneous structure are indistinguishable (i.e. at 1000 magnification) from each other with the exception of a few interfaces of discontinuity in some specimens. This indicates that the layers have most likely continued the structure with fine grains persisting. This characteristic factor of successive layers of Cu being indistinguishable from each other has been demonstrated in most of the specimens produced with the various cathode speeds. However, referring back to the Cu-Cu curve in figure 4, it is shown that the slope is not too great from one extreme point to the other. A confirmation of this small change in hardness is the similarity of the microstructures of Cu for the relative specimens in figure 5b, 5c, 5d, and 5e. If such grains were more precisely resolved one should find that a slight decrease in grain size exists which accompanies the slight increase in hardness for Cu-Cu structures.

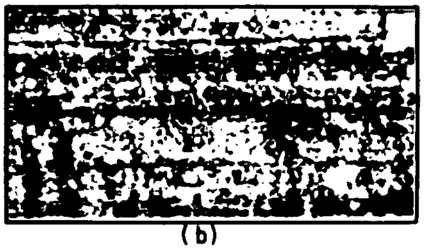
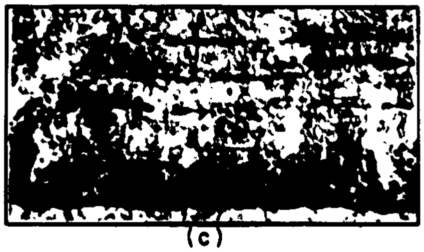
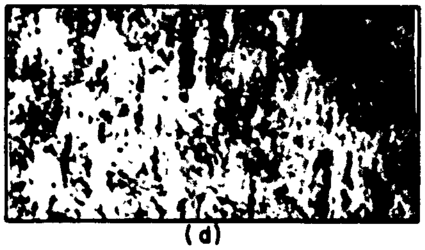
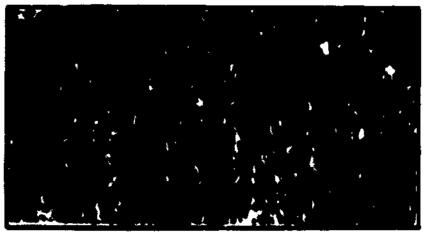
Ni-Ni Structure

Figure 6(a) shows the typical structure [5, 10] of a conventional sulphamate Ni deposit measuring a hardness of 195 Knoop which was produced by the same conditions given for conventional Cu (i.e. deposited on a stationary cathode).

	CATHODE SPEEDS IN RPM	KNOOP HARDNESS	ETCHANT
 (a)	STATIONARY (CONVENTIONAL DEPOSIT)	57	50ml. NH_4OH 20ml. H_2O_2 (3%) 50ml. H_2O (approx. 10 sec.)
 (b)	4.61	146	SAME AS (a)
 (c)	16	148.6	HNO_3+CH_3COOH (50:50 Conc.) (30 sec.)
 (d)	64	149	
 (e)	92	132	

CROSS SECTIONS OF COPPER STRUCTURES
(1000 MAGNIFICATION)

FIGURE 5

	CATHODE SPEEDS IN RPM	KNOOP HARDNESS	ETCHANT TIME
 (a)	STATIONARY (CONVENTIONAL DEPOSIT)	195	2 $\frac{1}{2}$ MIN.
 (b)	4.61	396.6	9 $\frac{1}{2}$ MIN.
 (c)	16	419	2 MIN. 50 SEC.
 (d)	64	356	10 SEC.
 (e)	92	385	5 SEC.

CROSS SECTIONS OF NICKEL STRUCTURES

1000 Magnification Etchant: $HNO_3 + CH_3COOH$ (50:50 Conc.)

FIGURE 6

The microstructures and hardnesses of successive layers of Ni on Ni with various cathode speeds, plated with the conditions given in (b) are shown in figure 6b, 6c, 6d and 6e. These Ni-Ni structures are varied somewhat and their hardness are shown to be governed by the existence of interfacial boundaries that have been resolved at 1000 magnification. To clarify the point, it may be stated that zones with an increasing number of resolved interfacial boundaries and subsequent grain refinement results in high hardness readings. Zones that show no existence of multi-layers, but rather a continuation of grain growth which is coarsened and clearly resolved, result in lower hardness readings. With this governing factor in mind, one can easily perceive the inconsistent effects of cathode speeds on hardness, by a close examination of the photomicrographs for Ni-Ni structures in figure 6. It seems plausible that the zones, showing sharp demarcations of interfaces, have resulted due to: (1) a structure which promotes discontinuity of grains, or (2) an oxide or other compound formation of unknown origin on the surface of the layer. This layer offers a foreign substrate which influences the succeeding deposition of Ni and results in an arrangement of atoms in a state of strain. This surface condition influences size and shape of crystals of subsequent nickel layers.

A number of factors related to these interfaces which may contribute to the high hardness measurements are: (1) adhesive strengths greater than the cohesive strength of the substrate and of the succeeding deposit, (2) formation of a hard alloy or compound at the interface, (3) a profound change in the crystal structure and subsequent grain refinement (one of the most likely factors), and (4) the existence of high residual tensile stress in the thin layers. However, great caution should be taken in correlating stress with hardness [11, p. 33]. One may best conclude that a combination of these factors play a role in the property of hardness.

The Ni-Ni curve shown represents average hardness of selective structures, possessing comparable interfacial characteristics in their microstructures, since it is evident that structures with continuous interfaces would increase in hardness with decreasing thickness of single layers. For this reason, the curve is shown with a broken line.

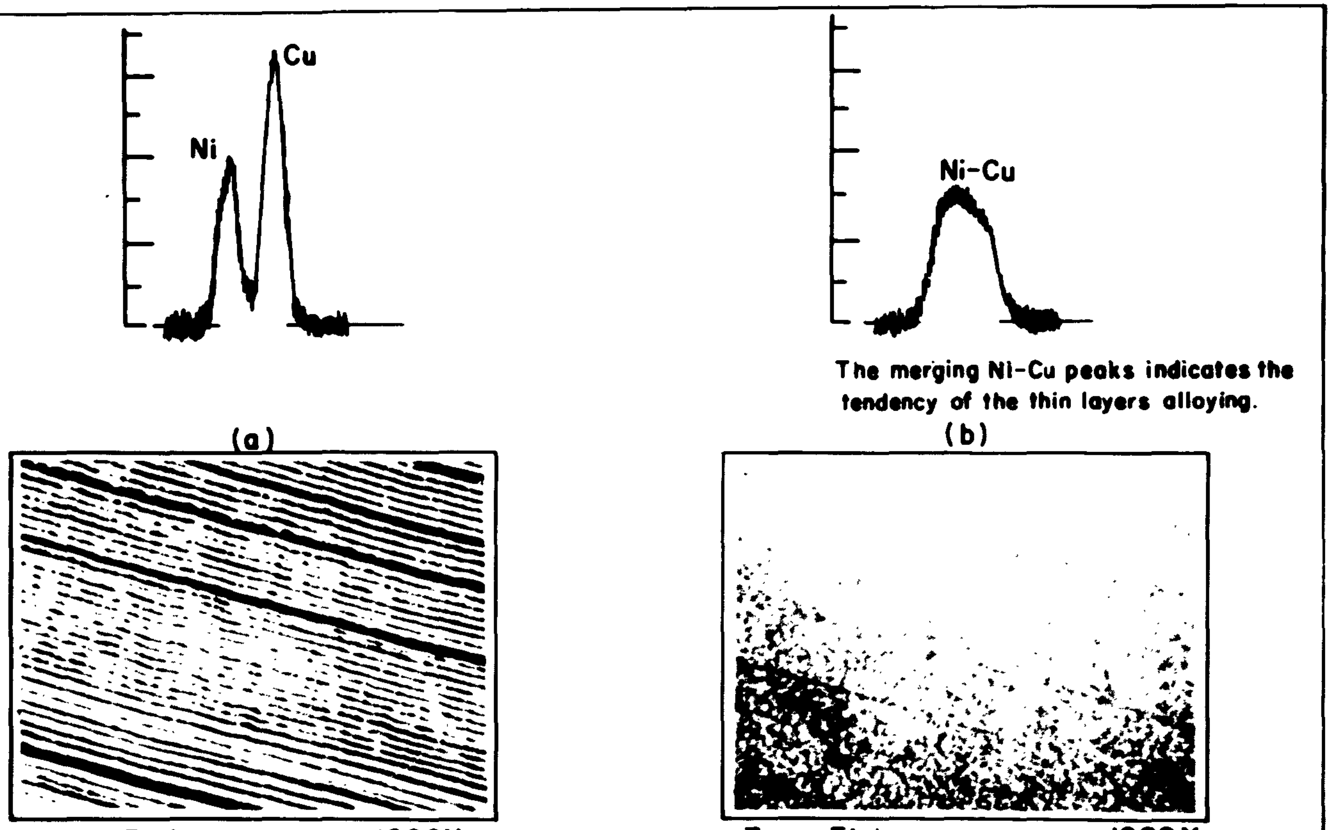
The large dispersion of hardness readings and inconsistent microstructural changes with the Ni-Ni structures was also experienced with the Fe-Fe. Therefore to avoid further confusion, a hardness plot of the Fe-Fe system has not been drawn. However, this disperion of hardness and the discontinuous interfacial boundaries in the microstructure does not occur when alternating one metal coating with another.

Ni-Cu Structures

We now have a general idea of the changes that take place in crystal structure and approximate hardness of single metal structures of Ni and Cu through the employment of the dual cell device with the rotating cathode using various speeds. These banded structures of Ni-Ni become of great interest, in view of the examples and different causes of banding of single bulk layers cited by Diggan[10] and by Blum and Meyers [11, p. 41-42]. From the data examined, however, it can generally be concluded that a structural change of the layers takes place in comparing deposits on a stationary cathode to deposits on a rotating cathode which interrupts the plate. This change from outward to lateral growth should be conceivable with the dual cell principle with various cathode speeds which influences the size of the crystals. These results of a fine grain size are in accordance with the chief governing factors established by Finch [12] and others.

Figure 7 shows photomicrographs and corresponding x-ray diffraction intensity peaks of multi-layered structures of Ni-Cu for two cathode speeds. These structures produced at cathode speeds of .86 rpm and 92 rpm offer an appreciable difference in their thicknesses of single constituent layers (Table I) for a good evaluation study. Results show that the micro-etched Cu layers produced with a cathode speed of .86 rpm are clearly distinguishable from the Ni layers but the layers produced at 92 rpm are not resolvable at the 1000 magnification.

The x-ray diffraction curves for the structure produced at .86 rpm show fairly sharp intensity peaks distinguishing the Ni and Cu layers. However, the layers produced with a cathode speed of 92 rpm shows a relatively diffuse x-ray diffraction intensity curve. This occurrence is recognized as an alloying tendency of the Ni-Cu layers through interdiffusion. In clarifying this, it may be stated that a third phase, consisting of a solid solution of Ni and Cu, is existing in the system with pure Ni and pure Cu. The possible causes for diffusion of the layers in this case may be many such as stress, thermal, and possible surface oxide concentration gradients. It may also be possible that interdiffusion exists in structures consisting of thick layers, but would not be detected by x-ray diffraction. This failure of detection by diffraction seems reasonable because the interdiffused layers could be a small percentage of the thick layered structures which have less interfaces. However, any conclusions from this study on such causes would be purely speculative, since the mechanism by which diffusion occurs in substitutional type alloys in this case cannot be clearly answered.



The merging Ni-Cu peaks indicates the tendency of the thin layers alloying.

10 sec. Etch 1000X

Cathode Speed-.86 RPM

7 sec. Etch 1000X

Cathode Speed- 92 RPM

note: layers are indistinguishable

Etchant · $HNO_3 + CH_3COOH$ (50:50 Conc.)

CROSS SECTIONS & X-RAY DIFFRACTION PEAKS (111 PLANES) OF TWO MULTI-LAYERED Ni-Cu SYSTEMS (AS PLATED)

FIGURE 7

Since the hardness curve for Ni-Cu in figure 4 has been plotted with a sudden drop off at the point corresponding to specimens produced with cathode speeds of 92 rpm, an explanation seems warranted. Close examination of the data on hardnesses for specimens produced with 92 rpm cathode speeds consistently showed average readings lower than specimens at 64 rpm. It is recognized that such differences, in hardness readings are no greater than hardness variations which are sometimes encountered with measurements of the same specimen. In view of the alloying tendency shown by the x-ray diffraction data it seems reasonable to consider this hardness a characteristic change. This characteristic hardness fall-off is even more pronounced with the Ni-Fe system (figure 4). However, no x-ray data was available to confirm the relationship of interdiffusion with this hardness fall-off for Ni-Fe.

One may expect such interdiffusion to result in an increase in hardness through solid solution strengthening, rather than a decrease in hardness. However, intermetallic compounds which may exist at the interfacial boundaries of structures, in the absence of interdiffusion of the multi-layers, would contribute markedly to the increase in hardness.

To substantiate our conclusions on this hardness change it is conceded that more data with these speeds and also data with higher speeds are required.

Data on As-Plated Multi-layers

The range of cathode speeds of .33 rpm to 92 rpm were selected to provide structures consisting of a considerable range of single layer thickness (Table I) which were desired for this study. Some specimens produced at 64 and 92 rpm, experienced spontaneous cracking of the multi-layered structures during plating and in a few cases after plating. This problem undoubtedly stems from the existence of very high residual tensile stresses in these layers. Since the one set of plating conditions was strictly adhered to in our investigation, no corrective action was taken to alter the condition. However, such cases were few and fortunately did not restrict the examination of specimens produced at these cathode speeds (i.e. 64 and 92 rpm).

Diffusion of Multi-layers

Alloying by diffusion through heat treatment of multi-layered structures produced with the dual cell is the subject of a more advanced study. However, it was decided to explore one area of this study with the Ni-Cu system. The Ni-Cu system seems to be one of chief interest and somewhat simple for alloying, since nickel and copper are completely soluble in each other, are both F.C.C. in structure, have atomic diameters favorable for diffusion and should form a single phase substitutional type solid solution.

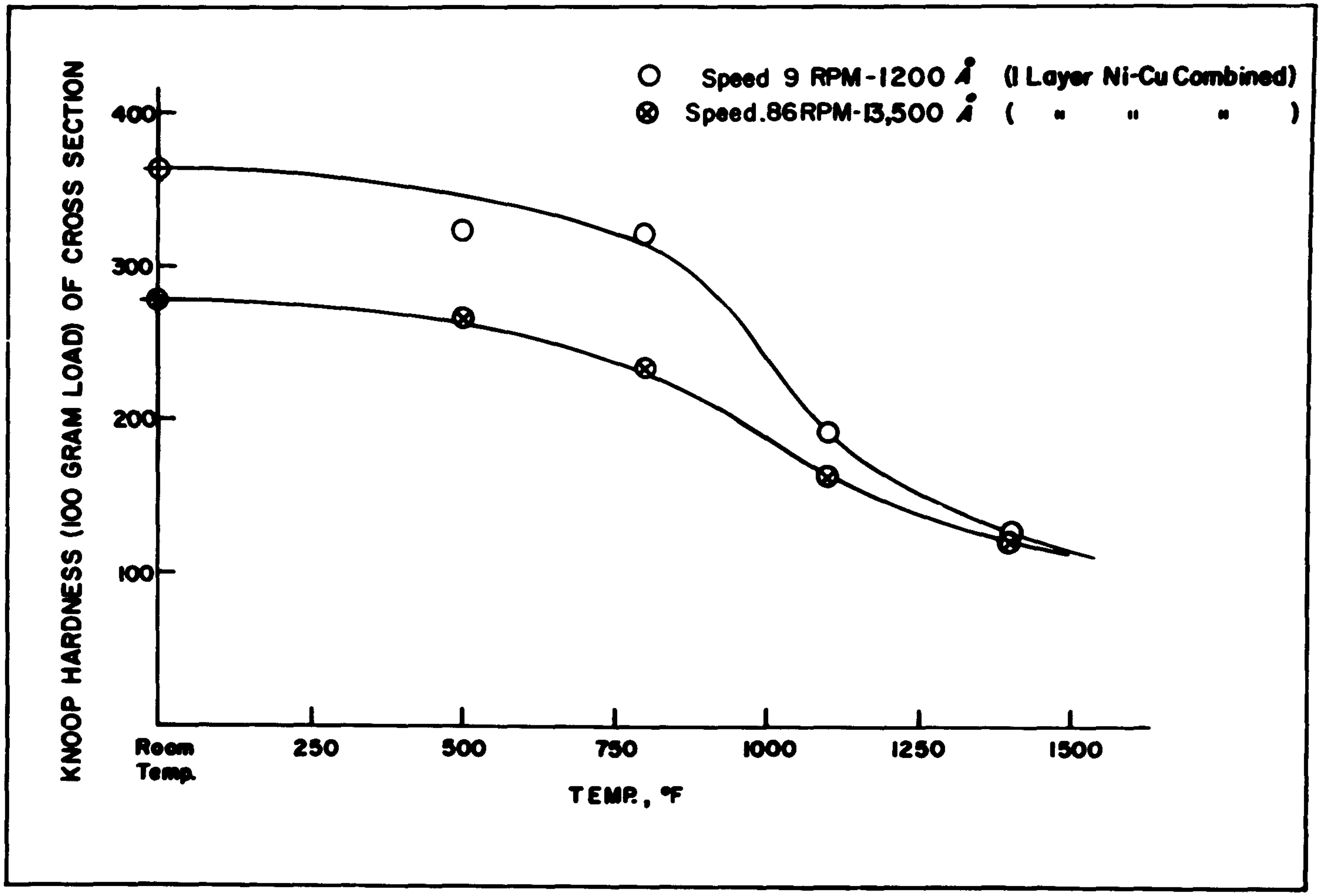
Two multi-layered specimens of Ni-Cu which were produced with two different cathode speeds and then subjected to various temperatures were investigated. The calculated layer differences in the two structures are given in Table II. These layer differences were chosen because they were both somewhat resolvable at 1000 magnification and would provide interesting specimens for metallographic and also x-ray diffraction studies in observing the microstructure and phase changes.

TABLE II
CALCULATED LAYER DIFFERENCES OF TWO NI-CU SPECIMENS

Specimen	Cathode Speed	Thickness of Ni layers	Thickness of Cu layers
1	0.86 rpm	8,100A°	5,400A°
2	9 rpm	722A°	478A°

The two multi-layered coatings of .006 inches overall thickness were removed from their cathode cylinders and each cut into 5 equal strips. Then the strips from the 2 specimens were paired (1 from each specimen) and subjected to temperatures of 500, 800, 1100 and 1400°F with the remaining pair retained for room temperature evaluation. The strips were heated at the specified temperatures for 15 minutes in an argon atmosphere (i.e. flowing slowly through the furnace), followed by furnace cooling. The temperatures were measured with a thermocouple mounted inside and located close to the specimens which were suspended freely.

Following this procedure, a small section from each strip was cut for metallographic and hardness studies and the remaining portion of the strip was used for examination with the x-ray diffraction unit. The results from the hardness measurements for the two specimens have been plotted and shown in figure 8. Although, it would seem difficult to determine the recrystallization point, in view of the two metals (as-plated) existing in the system as a mechanical mixture, both curves show this point of recrystallization to be somewhere under 500°F. However, our interests in this comparative study



HARDNESS vs TEMP. OF TWO MULTI-LAYERED Ni-Cu SYSTEMS AFTER HEATING FOR 15 MIN. IN AN ARGON ATMOSPHERE

FIGURE 8

were to examine the solid-state phase changes taking place for the various temperatures of the two as-plated systems (i.e. the .86 rpm and 9 rpm specimens).

Figures 9 and 10 show the resultant microstructures, hardnesses and corresponding x-ray diffraction peaks of the two multi-layered systems after heat treatment. These diffraction peaks represent the (111) planes since they are the planes of highest intensity for both Ni and Cu. A close examination of the results for both specimens clearly reveals the expected faster rate of phase change for the specimen with the thinner layers (i.e. 9 rpm) as compared to the thicker layers produced at a cathode speed of .86 rpm.

Some of the interesting points that should be noted are:

Figure 9 (.86 rpm Specimen)

The sharp x-ray diffraction intensity curve (figure 9d) indicates that complete interdiffusion takes place at approximately 1100°F. However, the corresponding microstructure shows a faint appearance of layers still evident. This could be due to the structural arrangement of the original layers of relatively greater thickness.

Figure 10 (9 rpm Specimen)

a. The microstructure corresponding to the 500°F treatment, reveals discontinuity of copper layers (dark) which indicates some diffusion has taken place.

b. In reference to the as-plated microstructure for this specimen, etching difficulties, again apparently due to changes in chemical resistance, were encountered in attempting to reveal the layers resulting in a dark view. This problem did not occur with the specimen treated at 500°F, which shows a clear contrast of the existing layers.

c. Complete interdiffusion, as indicated by the x-ray diffraction pattern, (figure 10b) seems to occur just above 800°F. In looking at the hardnesses given under the corresponding microstructures, a large decrease occurs after the 1100°F treatment.

d. The microstructure corresponding to the 1400°F treatment offers a good example of increased grain growth.

This initial study on the interdiffusion of multi-layers offers a general idea of the behavior of such structures.

Studies have not yet been conducted with multi-layered structures that consist of much thinner layers (i.e. above 92 rpm) where the required temperatures and times for interdiffusion should be much lower. It seems evident from existing data that complete alloying will occur during plating when the rotating cathode is increased to some optimum speed.

ACKNOWLEDGEMENT

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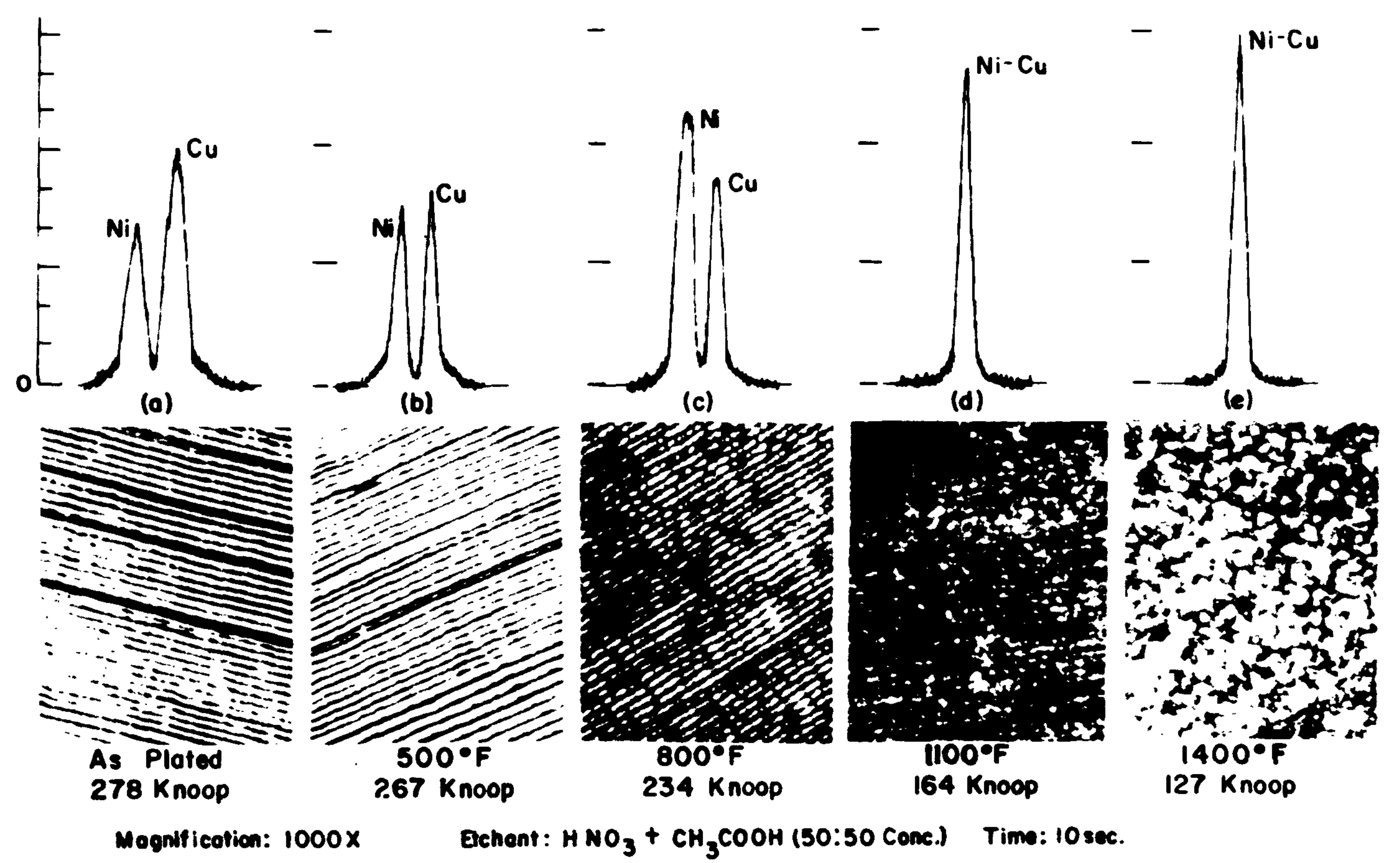
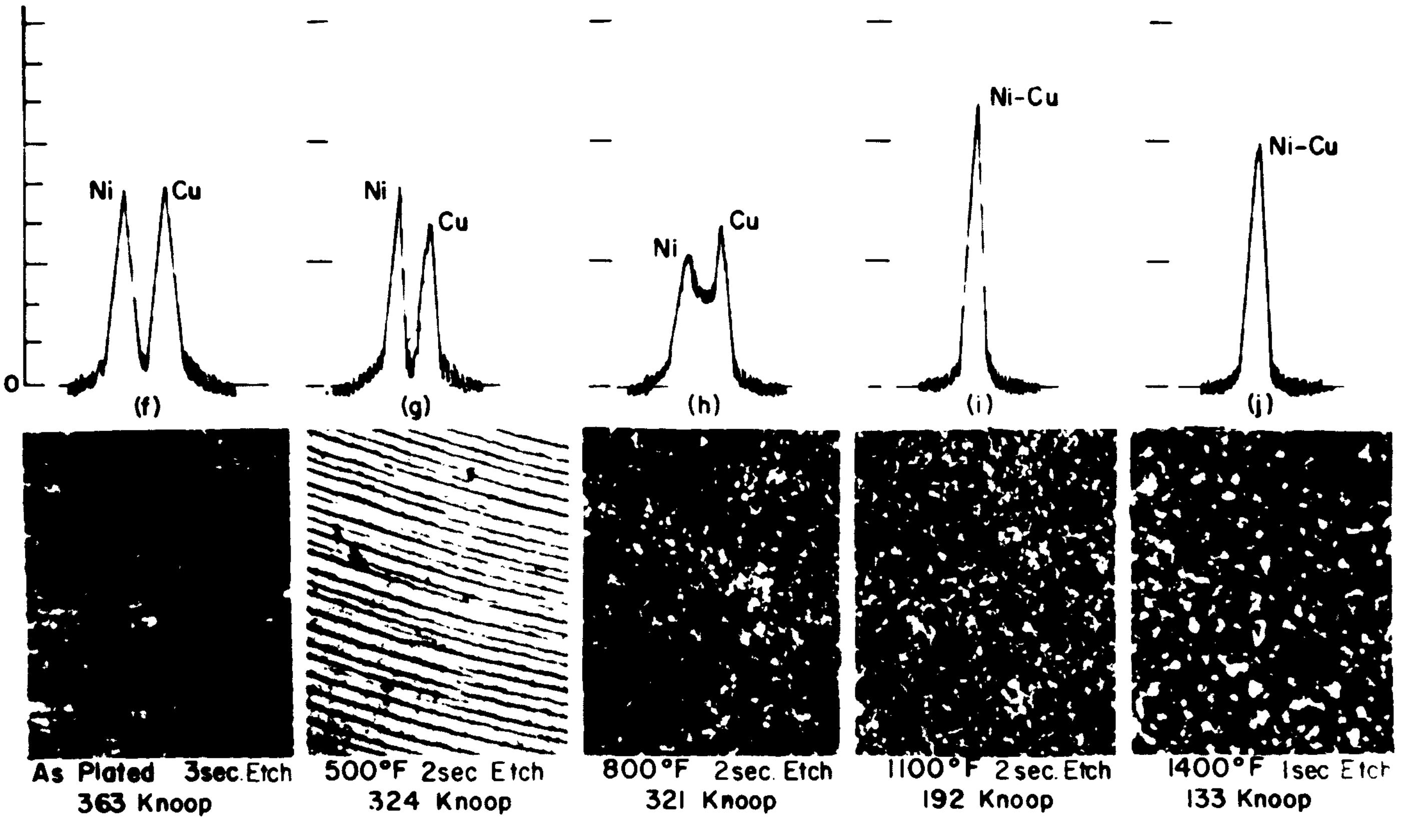


MICRO-STRUCTURES & RELATED X-RAY DIFFRACTION PEAKS (111 PLANES) OF A MULTI-LAYERED Ni-Cu SYSTEM SHOWING STAGES OF ALLOY FORMATION AFTER HEATING FOR 15 MIN. AT DIFFERENT TEMPS. IN AN ARGON ATMOSPHERE.

(1 LAYER OF Ni-Cu COMBINED IS 13,500 Å THICK (SPEED .86 RPM))

FIGURE 9



Magnification: 1000X Etchant: HNO_3+CH_3COOH (50:50 Conc.)@Time As Indicated in sec.

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(1 LAYER OF Ni-Cu COMBINED IS 1200Å THICK (SPEED 9 RPM))

FIGURE 10

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A DUAL CELL PLATING APPARATUS FOR DEPOSITION OF MULTI-LAYER METAL SYSTEMS by V. P. Greco

Report No. WVT-ID-6308, June 1963, 33 pages, 10 figures and 2 tables. DA Project No. 1-F-5-23801-A-289-02, OMS Code No. 5522.11.43902. Unclassified Report

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Data compiled has shown that:
lamellar structures exhibit increasing hardness and smoothness with decreasing thickness of single constituent layers (approximate layer thickness range

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