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EVALUATION
OF
CARBONYL NICKEL

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ABSTRACT

Four samples of nickel deposited by the carbonyl process are examined for hardness, strength, porosity, microstructure and chemical composition. Results are compared with reported values for electrodeposited nickel.

Four distinct types of microstructure exhibited by the four samples are examined and probable process variables are assigned as causes.

CARBONYL NICKEL EVALUATION

I. INTRODUCTION

The purpose of this study was to examine the mechanical, chemical and physical properties of carbonyl nickel, to compare these properties with those of electrodeposited nickel and to determine the inherent advantages and limitations of the carbonyl nickel process. Four separate samples were considered. The samples are shown in figures 1 and 2.

Figure 1. (a) (b) Nickel Plated Aluminum Cylinders. (c) Segment of Nickel Annular Ring. All samples shown approximately actual size.

Illustrated by (a) and (b) are transverse and longitudinal sections respectively, of nickel plated aluminum cylinders, while (c) is a section parallel to the direction of grain growth taken from an annular ring.

The fourth sample shown in figure 2, was furnished by Commonwealth Engineering of Dayton, Ohio. It was a 6-inch diameter disk, $3/16$ -inch thick with 5 concentric annular projections. These projections are shown as dashed lines in figure 2.

Figure 2. Nickel Plated Disk.

Five tensile specimens and two hardness strips were cut from the regions indicated in figure 2. The numbers on the hardness strips represent test points. The tensile specimens were machined according to figure 3.

Figure 3. Machined Specimen From Nickel Plated Disk.

II. HARDNESS

Values obtained for the samples illustrated by (a), (b) and (c) of figure 1 are shown opposite hardness indentation marks in the photomicrographs in figures 4, 5 and 6.

Figure 4. Nickel Over Aluminum Cylinder. Transverse Section - 50X.

	KNOOP HARDNESS 500 GRAM LOAD	CONVERTED TO R_c	
1.	151*		
2.	243	16.5	
3.	345	32	
4.	325	29	
5.	235	15	
6.	296	25	
7.	252	17	
8.	201	6.5	
	271	20	Average

* Not included in Average

Aluminum
Mandrel →

Figure 5. Nickel Over Aluminum Cylinder. Longitudinal Section - 50X.

	KNOOP HARDNESS 500 GRAM LOAD	CONVERTED TO R_C	
1.	243	16.5	
2.	255	18	
3.	255	18	
4.	255	18	
5.	241	16	
6.	243	16.5	
7.	243	16.5	
8.	271	20	
9.	292	24	
10.	<u>232</u>	<u>14</u>	
	253	17	Average

Figure 6. Section of Nickel Annular Ring - 14X.

As illustrated in figure 4, the third test from the outside edge was made just inside a phase change region in an area of very fine grain structure. All other readings were extremely close to one another. Overall average hardness was R_C (Rockwell Scale) 14.

Figure 5 exhibits an extremely soft outer and inner edge. The inside layers exhibited a varying hardness with an average of R_C 22.5. The number of layers in cylinder samples (a) and (b) are different because they were plated at different times.

Figure 6 illustrates a multitude of uniform lamellar bands across the bottom of the microsection, a region of indistinct lamellar bands in the middle, and a very fine grained columnar growth toward the outside edge. This specimen exhibited a very uniform hardness across the section with an average of R_C 17.

The arithmetic average R_C hardness values for figures 4, 5, and 6 were R_C 14, R_C 20 and R_C 17 respectively, which shows that the two cylinders differed considerably and the value for the annular ring segment fell in midway.

Information pertaining to two types of electrolytic nickel baths that produce nickel with properties roughly comparable to carbonyl nickel is shown in table 1.

With reference to table 2, the hardness of the three samples shown in figures 4, 5 and 6 fall within the range given for deposits produced from the sulfamate bath. Reference to other properties listed will be made later.

TABLE 1							
REVIEW OF ELECTROLYTIC NICKEL BATHS COMPARABLE TO THE CARBONYL NICKEL PROCESS							
Type and Nominal Composition (Oz/Gal)	pH	Temp. °F.	Normal C. D. a/ft ²	Typical Mechanical Properties			
				Internal Stress psix10 ⁻³	Hardness R _c (Vickers)	Elong. % in 2 in.	Ult. T.S. psix10 ⁻³
<u>Chloride</u> (1) a. Nickel Chloride -- 40 Boric Acid ----- 4	2	130-150	25-100	40	19-21 (230-240)	20	98.9
(2) b. Nickel Chloride -- 32 Boric Acid ----- 4 (Cobalt Free)	3	131	53.8	37	18 (228)	17	97
(2) c. Nickel Chloride -- 32 Boric Acid ----- 4 (0.96% Cobalt)	3	131	53.8	42	22 (244)	14	102
(1) <u>Sulfamate + Cl (-)</u> Nickel Sulfamate - 40 Nickel Chloride --- 4 Boric Acid ----- 4	3.5-4.2	75-160	20-140	13-18	12-23 (200-250)	5	94-108

TABLE 2			
RADIAL HARDNESS STRIPS - A & B FROM 6" DIA DISK			
<u>Hardness Strip</u>	<u>Position</u>	<u>Rockwell-Superficial Hardness 45 N</u>	<u>R_C (Converted)</u>
A	1	24	23.5
	2	22	21.5
	3	27	26.0
	4	24	23.5
	5	23	22.5
	6	24	23.5
	7	26	24.0
	Avg.	24	23.5
B	1	23	24.0
	2	26	24.0
	3	24	23.5
	4	25	24.0
	5	25	24.0
	6	23	22.5
	7	23	22.5
	8	22	21.5
	9	27	26
	Avg.	24	23.5

TABLE 3		
HARDNESS ACROSS SECTION 6" DIA DISK		
<u>Position</u>	<u>Knoop Hardness 500 gm Load</u>	<u>R_C Converted</u>
Mandrel	363	35
Center	289	24
Outside Edge	271	20

The readings listed in tables 2 and 3 are from a section made parallel to the direction of grain growth. The values in table 2 were made in the middle of the 3/16 inch thickness and resulted in arithmetic average hardness of R_C 23.5 for both strips. A small piece from one strip was microsectioned and checked for hardness across the 3/16 inch thickness. The greatest hardness, R_C 35 as shown in table 3, was close to the mandrel. A finer grain structure was found in this region of initial deposition. The entire coating was a single deposit with no interface separations like the cylinder specimens. The hardness gradient going from hard, close to the mandrel edge, to soft near the outside edge is the characteristic of this specimen alone. It is possible that this condition could repeat itself for other deposits.

Generally speaking, the single phase deposit with an average hardness of approximately R_C 24 was harder than various multilayer deposits with an average hardness of R_C 17. Available literature indicates a general range of R_C 21-26 to R_C 13-30 for fine columnar, dendritic or fine grained structures and R_C 24-30 for fine structures without any visible growth pattern.^{3,4} Using the average values quoted in table 2 for comparable electrodeposited nickel, it appears the carbonyl nickel is at the high side of the hardness ranges, as strength values may be expected.

III. GRAIN STRUCTURE AND POROSITY

The four specimens under consideration were all subjected to a metallographic analysis. The sample, taken from the disk, was also x-rayed. The x-rays showed the disk to be free of any voids or inclusions per normal ASTM acceptance standards. The only exception to this was that the annular projections on the disk were found to be hollow. A sketch of these projections is shown in figure 7.

Figure 7. Section of Six Inch Disk Shown In Figure 2.

A photomicrograph of a typical void inside the small ridge is shown in figure 8 with the grain growth having progressed parallel with the longest dimension of the void.

Figure 8. Void In Projection On Six Inch Diameter Disk. 50X - 1 Division Equals 824×10^{-6} Inch.

The open defect shown in figure 8 is approximately .033 inch long by .002 inch wide and is naturally smaller than the comparable faults found in the .090 ridge. Of particular interest is the manner in which the hole progressively plated shut and the associated grain growth needles. It is a safe assumption that any plated part with similar positive features would exhibit the same type of defect. It should be noted that the fault extended all the way through the plating thickness, extending to the right from the void in figure 8, thereby seriously affecting the strength characteristics as will be illustrated later.

The samples examined exhibited four different types of coatings:

1. A single, uninterrupted deposit.
2. A distinct, multilayer deposit with each layer a different thickness, approximately .004 to .016 inch.
3. A distinct, multilayer deposit with all layers roughly the same thickness and individually thin, approximately .0003 to .0008 inch.
4. A multilayer deposit with very indistinct, diffused boundaries, at times approaching the appearance of (1) above.

The first type of deposit comprised the structure of the 6-inch disk shown in figure 2. Representative photomicrographs of the structure are shown in figures 9 through 11.

Figures 9 and 10 are both microsections parallel to the direction of grain growth, with the growth progressing in a vertical direction.

Figure 9 at 250X, clearly shows a very fine columnar growth pattern with associated growth needles. Figure 10, taken at 1000X, still fails to show the individual grains which are estimated to be 0.4 microinch.² Obviously a uniformly fine structure such as this would have very low porosity. Literature indicates an open porosity, obtained by standard methods, whose volume does not exceed 1 to 1.5 percent of the deposit.³ In coatings greater than 400 microinch, the coating is either pore free or with a very few single pores.⁵ In coatings thinner than this, the porosity increases sharply. Figure 11 shows an equally fine structure in a microsection taken transverse to the direction of growth. It is generally conceded that the porosity of carbonyl nickel is of the same magnitude if not less than that of electro-deposited.^{6, 7} Note the contrast between a typical electrodeposited structure as exhibited in figure 12 with that of figure 9.

Figure 9. Single Layer Deposit - Parallel Section - Six Inch Disk - 250X.

Figure 10. Single Layer Deposit - Parallel Section - Six Inch Disk - 1000X.

Figure 11. Single Layer Deposit - Transverse Section - Six Inch Disk - 1000X.

Figure 12. Electrodeposited Coating - As Plated Test Piece - Parallel Section - 100X.

The second type of coating, illustrated in figures 4 and 5, has several distinct layers of varying thickness obtained on plating the aluminum cylinders. Here the individual layer thicknesses vary from .004 to .016 inches with distinct physical separations at some of the interfaces.

The third and fourth types of deposits are exhibited by the annular ring sectioned in figure 6.

The distinctly layered region near the bottom of figure 6 is shown at a greater magnification in figure 13. The unusual layer uniformity

Figure 13. Multi-layer Deposit -
Parallel Section - Annular Ring -
250X.

indicates that this was deposited by a closely controlled process. This was done by introducing a specific amount of nickel carbonyl gas into the decomposition chamber, allowing the process to run until the gas was depleted, purging the chamber of the spent charge and injecting a fresh charge. It should be noted that for the wide, narrow and indistinct layers, the growth within the individual bands was columnar. Across the micro-section of the deposit of the annular ring shown in figure 6, three different types of growth structures were exhibited.

- (a) The individually thin, fairly uniform multiple layer deposit shown in figure 13 with an actual physical separation at the interfaces.
- (b) A deposit very similar to the one in (a) except the boundaries are less distinct with growth needles occasionally extending across the interfaces to actually connect the adjacent layers. No heat treatment was used to achieve this effect. Therefore, a growth needle started in one layer continued to grow during the next cycle.
- (c) The last type of deposit is the next logical step beyond (b), in that the individual layers have become so well bonded together as to almost appear to be the result of an uninterrupted process.

A banded structure such as this can also be achieved by introducing oxygen in short bursts to the plating chamber or continuously adding a small amount of oxygen during the entire process.⁴ The first method will result in many small, even bands with a hardness of approximately R_C 40. The second process will give wider, indistinct, less even bands with a hardness of approximately R_C 62. Since the hardness ranges of both of the banded structures were well below the quoted values for the alternate processes, it can be assumed that oxygen, introduced either intentionally or otherwise, was not the cause of the banding.

IV. INTERFACE AND MANDREL BONDING

The interfaces between layers in specimens shown in figures 4 and 5 are shown at a greater magnification in figure 14.

Figure 14. Interface Bonds -
Nickel Over Aluminum Cylinder -
Transverse Section - 250X.

The photomicrograph shows two distinct types of interfaces between plated layers. At the bottom is a closely knit bond somewhat diffusional in nature, while the other is definitely a rather poor bond showing an actual physical separation. It is hard to explain this separation except to say that perhaps the temperature of the mandrel and the predeposited nickel layers fell below optimum. It is unlikely that surface contamination would be a problem at this stage of the process.

Achieving a satisfactory bond between the base metal and the deposited nickel is somewhat difficult. A layer of adsorbed gases and the presence of foreign material on the plating surface seem to be the prime causes of poor adhesion. The effective removal of this layer may be achieved in several ways. Extreme care should be taken not to contaminate the cleaned surface prior to plating.

Adhesion may be improved by applying some of the following steps prior to carbonyl plating.

- (a) Anneal the specimen at 430 to 480 degrees Centigrade for 15 to 30 minutes in an inert or reducing atmosphere to remove the adsorbed layer.⁸
- (b) Mechanically abrade the plating surface.
- (c) Nickel flash of .0002 to .006 inch on the plating surface.
- (d) Vapor degrease and vacuum outgas the specimen.

After plating, a diffusional bond may be obtained by heating in hydrogen or some other inert atmosphere at 550 to 700 degrees Centigrade for 30 minutes.

Opinion is varied on whether or not mechanical abrasion has any value in improving the bond. Bonds obtained by this means are shown in figures 15 and 16.

At the bottom of figure 15 is seen the bond achieved on the plated aluminum cylinder shown in figure 1 (b). The fact that good adhesion was obtained is shown in figure 16. In the process of sectioning the cylinder transversely, the bond was ruptured by tearing away a section of the base metal that adhered to the nickel coating. Upon close examination, the mechanical bond that held can be seen intact at the center of the ruptured chip. Owen states that the strength of the bond depends on the base metal, and that the highest degree of adhesion obtained was to copper.⁴ Attempts to peel the coating off the copper caused a rupture similar to that shown in figure 16. He further stated that nickel bonded to aluminum inconsistently and with moderate adhesion, to brass with a weak to moderate bond and to steel with a weak bond. It is possible that some of the suggested methods of improving the adhesion previously mentioned might alter this order of bond strength.

Figure 15. Nickel Over Aluminum Cylinder - Mechanical Inter - face Bond - 250X.

Figure 16. Nickel Over Aluminum Cylinder - Fractured Inter - face Bond - 250X.

V. MECHANICAL PROPERTIES

The tensile specimens shown in figures 17 and 18 were machined from those regions of the disk shown in figure 2 in accordance with dimensions given in figure 3. Mechanical properties were obtained as given in table 4.

TABLE 4				
MECHANICAL PROPERTIES				
Speciman Number	Yield Point at 0.2% Offset PSI	Ultimate Tensile Strength PSI	Elongation %	E, Young's Modulus, Initial Tangent PSI
1	*	44,000	0	*
2	91,000	106,000	3	34,000,000
3	89,000	120,000	5	33,000,000
4	*	33,000	0	*
5	74,000	115,000	14	29,000,000

The premature failure of specimens 1 and 4 was due to the plating faults shown in figure 7. Figures 17 and 18 show the manner in which these two specimens failed. The three remaining specimens produced strength characteristics in the expected ranges, especially when compared with the average values quoted in table 1. Except for number 3, these specimens also exhibited fractures typical of a ductile material, which is concurrent with the medium hardness of the metal as previously determined (Average R_C 23.5 - See table 3). Although it was not possible to obtain elongation values for samples 1 and 4, it is generally understood that laminated coatings caused by plating interruptions are not usually brittle.⁴

Unfortunately, the elongation values were too inconsistent and the sample too small for any meaningful conclusions to be drawn. Considering strength and hardness, the elongation should usually fall in the range of 5 to 14% as indicated by the chloride and sulfamate baths in table 1. The values for Young's modulus of 29-34 x 10⁶ psi compare favorably

Figure 17. Ruptured Tensile
Specimens From Six Inch Diameter
Disk - Specimens 1, 2 and 3.

Figure 18. Ruptured Tensile
Specimens From Six Inch Diameter
Disk - Specimens 4 and 5.

with electrodeposited nickel which is in the range of 30×10^6 psi to 30.5×10^6 psi.^{2,9} The sample is smaller than desirable, but further tests are planned.

An approximate linear relationship exists between the hardness and tensile strength of a material, and an inverse relationship between these properties and elongation since these measurements are all basically dependent upon the same general physical constants. As such, the general relationship of these characteristics as exhibited by the samples was compared with the like relationship for electrodeposited nickel. Assuming an average Vickers hardness of 250 for this sample, the A. E. S. Handbook indicates an elongation of 6% and a tensile strength of 107,000 psi. The handbook indicates an elongation of 6% for an assumed average tensile strength of 114,000 psi. This cross correlation, when compared to the limited experimental values, shows a very close agreement with conventional electrodeposited nickel.

VI. DENSITY

Density values were obtained from samples of the annular ring and the 6-inch disk and found to be 8.81 gm/cm³ and 8.68/8.72 gm/cm³, respectively, at 25 degrees Centigrade. These values compare poorly with theoretical values of 8.907 gm/cm³ for cast metal and 8.900/8.903 gm/cm³ for worked and annealed metal.² The density of nickel calculated from its lattice constant (3.5168kX units) is 8.91 gm/cm³.² Two samples were used in obtaining the limits for the 6-inch disk material. One sample included a plating fault and the other sample was without a plating fault. The difference in density was only 0.04 gm/cm³, which is negligible. Since so many unknown parameters were involved, no conclusions can be drawn as to why such low values were obtained. It appears that the very fine, multilayer ring sample was produced by a process that gave a better density than the process that produced the 6-inch disk. This statement should be qualified, since the number of samples analyzed were extremely limited.

VII. CHEMICAL COMPOSITION.

The chemical analysis shown in table 5 was determined from a sample of the 6-inch disk using an emission spectrograph.

TABLE 5			
CHEMICAL COMPOSITION			
	Test Results	(10) <u>Pure Ni (Electrolytic)</u>	(3) <u>Carbonyl Ni</u>
Ni + Co	99.825%	99.95%	99.78/99.88% (less Co)
Fe	0.088%	.01 / .04%	.02%
Cu	0.002%	.01 / .03%	
C	0.063%	Trace	0.1 / 0.2%
Si	0.001%	Trace	
S	0.030%	Trace	
Al	0.015%	-----	
Mg	0.003%	-----	
Carbonyl Ni ⁽³⁾ (Cont.) Mg + Si + P + S = 0.001% compared to .034% Co + Zn = 0.0005% compared to 0% Cd + Pb + Sb + Sn + Bi + Al = 0.0003% compared to .015%			

The sample tested was 0.125% less pure than commercially pure electrolytic nickel as defined by the American Electroplaters Society. Compared to electrolytic nickel, the sample had a higher iron content with somewhat comparable amounts of copper, carbon, silicon and sulfur. The aluminum and magnesium content was not indicated for pure nickel.

Compared to the Verbllovskii and Rotinyan values, this sample was found to fall within their general limits for the purity of carbonyl nickel. With the exception of carbon, cobalt and zinc, the impurity content was found to be higher. The carbon content, at 0.063% was considerably less than their range of 0.1/0.2%. No cobalt or zinc was found in this sample as compared with a 0.005% trace found in their sample.

In conclusion, it would be well to check several additional samples to determine if the figures given here are representative. Of particular interest would be verification of the carbon and iron content. Naturally, the emission spectograph gives no indication of the gaseous content (O_2 and H_2) of the deposit, which is a function of the purity of the Ni (CO)₄ gas and the overall efficiency of the system. It would be of great value to compare the gaseous content with that of electrodeposited coatings, which is approximately 0.0125% O_2 and 0.0009% H_2 . An analysis of this nature could be made by a vacuum fusion process in conjunction with a time-of-flight mass spectrometer.

VIII. PHYSICAL IMPERFECTIONS

During the investigation, several unusual features were found in the coatings. Some of these are shown in figures 19, 20 and 21.

Figure 19 illustrates an unusual feature found in the 6-inch disk specimen. The thin light band at the top of the photomicrograph is a nickel flash, approximately 40 microinch thick and separated from the parent metal deposit by a continuous void approximately .0005-inch wide. The irregularity in the middle is an inclusion probably caused by a particle of foreign material on the mandrel surface. It is recognized that the size of the physical separation as shown in the illustration may have been enlarged by the etchant, but its presence is undeniable. Since the carbonyl nickel process requires the absorption of heat, this may have been caused by allowing the mandrel temperature to fall below optimum just at the moment precipitation began. This flash was definitely not plated to the mandrel prior to the carbonyl process to improve adhesion. Instead, it was an accidental result of the carbonyl process itself.

Figure 20 shows two of the very few inclusions found in the multiple layered annular ring deposit. From the positions of these two particles, imbedded in the body of the deposits, it is likely they were introduced through the stream of carbonyl gas. On the other hand, particles sometimes are found at the interfaces of nickel layers produced by an intermittent process. An example of such an inclusion is shown in figure 21.

Figure 19. Nickel Flash and Separation Exhibited By Six Inch Disk - 500X.

Figure 20. Inclusions In Annular Ring Specimen - 1000X.

Figure 21. Interface Inclusion
Between First and Second Bands
of Nickel Over Aluminum Cylinder
At Corner of Longitudinal Section.

Notice the long, wide growth of needles of the first band projecting into the separation and the formation of a fine-grained structure as the second band started to deposit. The inclusion itself is approximately .004-inch long by .001-inch wide and, except for an attachment at the lower left-hand corner, lies entirely in the interface separation. To avoid these inclusions it seems necessary to maintain maximum cleanliness of the entire system, paying particular attention to the nickel carbonyl gas, and any carrier, diluent or purging gases.

IX. GENERAL DISCUSSION AND CONCLUSIONS

The deposition of nickel by the thermal decomposition of nickel tetra-carbonyl gas takes place in accordance with the following reaction:

A mandrel of the required shape is heated and exposed to a stream of the carbonyl gas at either reduced or atmospheric pressure. The nickel carbonyl gas, volatilized from a liquid, is often diluted with an inert gas, usually carbon monoxide. The optimum mandrel temperature appears to be in the range of 200 to 230 degrees Centigrade, although some sources report having obtained satisfactory coatings in the range of 270 to 310 degrees Centigrade. Maintaining an even temperature over the surface of the mandrel is difficult, while holding it at optimum temperature is of prime importance.

The rate of deposition, which is .005 inch to .025 inch per hour, is dependent upon the flow rate of the feed gas. A low flow rate will probably produce a finer grain structure than a high flow rate. The process can be run either continuously or intermittently, resulting in a single layer or multiple layer deposit, respectively. If an even coating is desired, the direction of flow with respect to the mandrel may be periodically reversed, with a resultant uniformity of thickness within 80 to 120 microinch.³

Considering tests conducted and literature consulted, the nickel carbonyl process has the following distinct advantages:

- (a) Strength, hardness and ductility properties generally equal to those of comparable electrodeposited nickel.
- (b) A high purity deposit.
- (c) Control over type of deposition and uniformity.
- (d) Porosity no worse if not better than electrodeposited coatings.
- (e) A rate of deposition approximately 10 to 15 times faster than that obtained electrolytically.
- (f) The capability of plating on nonconductors.

Some of the limitations include:

- (a) Requirement of post-deposition heat treatment to produce a satisfactory bond between deposited nickel and some base metals and at multiple layer interfaces.
- (b) Difficulty in maintaining an even, optimum temperature of the plating surface.

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