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**CORROSION POTENTIALS RESULTING FROM  
MICROSTRUCTURAL DIFFERENCES IN  
COMMERCIALLY PURE NICKEL**

**by**

**Harvey Hansen**

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A thesis submitted to the Faculty and the Board of Trustees  
of the Colorado School of Mines in partial fulfillment of the  
requirements for the degree of Master of Science in Metallurgical  
Engineering.

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## INTRODUCTION

### What is Corrosion?

Most of the metallic elements occur in nature as compounds, for example, iron as  $\text{Fe}_2\text{O}_3$  and copper as  $\text{Cu}_2\text{S}$ , while a small group of metals such as gold and silver are found in an atomic state. In basic chemistry we are taught that a reaction will take place only if a more stable compound is formed. From this it may be inferred that most of the metals are relatively unstable in an atomic state and tend to form more stable compounds.

The word "corrosion" as commonly used in scientific discussions today has taken on a more specialized meaning than is evidenced in Mr. Webster's dictionary, which states that corrosion is "an action of eating away by degrees." The reaction of zinc with 1 Normal HCl is not considered corrosion but rather "chemical reaction." The attack of sea water upon iron to form rust,  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , is termed "corrosion." The distinction is that corrosion denotes an attempt by a system, normally composed of a metal and an electrolyte, to reach a state of minimum free energy through "electrochemical action." Electrochemical corrosion, hereafter referred to simply as corrosion, involves anodes and cathodes separated by finite distances so that an electric current flows external to the solution.

Several theories have been advanced to explain the corrosion of metals, among them the acid (hydrogen ion) theory and the Nernst electrolytic solution pressure theory. The hydrogen ion theory has

few proponents today, and Nernst's electrochemical theory is now generally accepted as the best explanation based on current experimental evidence.

The Nernst theory assumes a definite tendency for a metal to change from its atomic to the ionic state. If electrically-connected metal grains having different electrolytic solution pressures are brought into contact with an electrolyte, the grain having the highest solution pressure will become anodic and will dissolve. This dissolution is accomplished by metal ions leaving the surface and entering the solution. As the metal corrodes, the concentration of its ions becomes greater and the tendency for more ions to enter solution decreases. Corrosion of the anode is accompanied by discharge of an equivalent number of cations and passage of an electric current, external to the solution, to the cathodic areas where usually hydrogen is evolved.

The speed at which corrosion proceeds is governed, in part, by the rate at which the reaction products are removed from the anodes and cathodes. The flow of electric current from the anodes to the cathodes will cease unless some means of hydrogen removal is effected. Hydrogen may be evolved as a gas, oxidized to  $H_2O$ , or oxidized to form hydroxyl ions. Oxygen gas, present in the atmosphere and in solutions exposed to air, is one of the most effective depolarizers known.

When insoluble compounds form at the metal-solution interface, corrosion is stifled or subsequently regulated by the rate at which the insoluble film is removed. Other factors governing the rate at which corrosion will proceed are: relative anodic and cathodic area, polarization, depolarization, hydrogen overvoltage, electrolyte



agitation, aeration of solutions, presence of galvanic couples, and the induced or residual stresses in the metal.

In the present study, fundamental investigations were made into the corrosion behavior of nickel metal prepared by different commercial processes and subjected to varying amounts of cold work. Any preliminary discussion of corrosion involving nickel must, of necessity, include some mention of passivity.

Two definitions of passivity are in common use today: 42/

1. The metal is passive if it behaves as though it had been transformed into a more inert material.
2. A metal is passive if it resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with its passage from a metallic state to appropriate corrosion products.

Passivity results from the formation of a protective film on a metal which has incomplete inner electron shells and energy bands 64/. These shells tend to fill with electrons and activate the metal. If an oxide film prevents the filling of the electron orbits, the metal is passive. Oxides form an adsorbing layer and trap any free electrons by covalent bonding, thereby retarding the flow of electrons from the metal-solution interface to the metal and so rendering the metal passive. An oxide film will also raise the polarization potential and thereby decrease the corrosion current flowing in the metal.

#### Why Potential Differences Exist on Metal Surfaces

Corrosion is considered to be a surface phenomenon. The surface

of a metal is in an unstable energy state because of the uneven distribution of the electron cloud near the surface 31/. The positive energy of the surface layer may express itself in various ways, several of which may result in corrosion.

Potential differences within a metal surface may be caused by:

1. Different crystal orientations
2. Grain boundaries
3. Inhomogeneity in composition
4. Size differences between grains
5. Macrostrains and microstrains
6. Difference in intensity of incident light
7. Uneven distribution of moisture over the surface
8. Presence of foreign substances on the surface
9. Nonuniformity of electrolyte
10. Differential aeration
11. Breaks in the protective film covering the metal.

Recent investigations with single crystals have shown that crystal faces oriented along different crystallographic planes have different free energies 64/. In some cases the measurable free energy of one face is five times that of an adjacent, differently oriented face. A metal grain in the surface so oriented as to contain more of these active planes than another grain should have a higher free energy and should become anodic when the surface is exposed to an electrolyte.

Grain boundaries are areas of high free energy because of the uneven distribution of electrons. Although the energy of a grain boundary depends partly on the energy of the grains adjacent to it, the boundary will always have a higher energy than the grains because

of its distorted structure 3/. The grain boundaries may under special conditions be small areas of extremely high energy and may therefore be subjected to severe intergranular corrosion.

Any composition differences or inclusions present in the surface of the metal will cause the formation of galvanic couples. Potential differences will exist between these regions just as they exist between the anode and cathode of a dry cell.

The process of solidification of a metal is not instantaneous. Some regions will have more fruitful collisions than others to form nuclei. The crystals which form first will grow at the expense of any smaller adjacent crystals since the smaller ones represent a higher energy state and are more unstable. After solidification is complete, some differences in size are still present. The small grains will still have a higher energy with respect to their larger neighbors, and so have a higher potential than their larger neighbors.

When metals are rolled, forged, or cold-worked in some other manner, energy is transmitted to the metal and locked up within it as residual stresses. Some grains will be more favorably oriented than others to slip and relieve these stresses. The grains which cannot slip will subsequently have a higher free energy than will the grains in which slip has occurred.

Why differences in exposure to light, uneven distribution of moisture, presence of foreign substances on the surface, non-uniformity of electrolyte, differential aeration, and breaks in the protective film covering the metal will cause potential differences has been discussed by many authors 6/, 36/, 53/, 57/, 64/, 65/, 68/, and will not be dealt with in this work.

## POTENTIAL MEASUREMENTS

### Object of Investigations

The primary purpose of the thesis work was to prove that potential differences do exist between grains in a commercially pure metal and to develop a technique for accurately measuring the magnitude of these differences.

After the differences in potential existing between grains had been evaluated, an attempt was made to correlate the magnitude of the potential differences with the degree of cold-work done on the metal.

It was qualitatively demonstrated that the grain boundaries are generally anodic to the grains and the smaller grains generally anodic to the larger grains.

The significance of the potential measurements in predicting the corrosion rates and the corrosion susceptibility of metals was then evaluated.

### Apparatus and Reagents

The following apparatus and reagents were used in the measurement of the potential differences existing on the surface of nickel metal:

1. Nickel metal in various commercial forms
2. Leeds and Northrup Type K-2 potentiometer
3. Leeds and Northrup optical galvanometer
4. Bausch and Lomb microscope and micrometer stage
5. Standard cell (potential = 1.01929 absolute volts)
6. Calomel half-cell ( 1 Normal KCl)
7. Two 1.5 volt dry cells
8. Glass capillary tubes
9. Pliofilm (pliolite) sheets and strips
10. Chloroform
11. Auxiliary equipment such as plastic tubing, copper wire, ringstands, bakelite mounting press, etching solutions.

### Technique Used to Measure Potentials

Specimen Preparation. The nickel specimen to be examined was polished and then etched with a solution of sodium cyanide and ammonium persulphate 45/. The cyanide-persulphate solution reacts slowly to etch the grain boundaries and inclusions black while leaving the grains light gray or in some cases unattacked. It should be noted that HCN fumes are given off when the solution is prepared; therefore reasonable care should be taken in using the etchant. Etching times vary from

5 to 15 minutes. Nitral was used successfully on some specimens, but it generally gave poor results and pitted the metal.

Plastic Coating. After the etching, the metal was coated with a thin transparent layer of plioform in chloroform. After drying by evaporation of the chloroform, the plastic insulated the entire specimen electrically.

The plastic solution was prepared by supersaturating chloroform with a modified isomerized rubber thermoplastic produced by the Goodyear Tire and Rubber Company under the trade name of plioform. The excess solid plastic was removed from the chloroform and the solution poured over the metal. A thin, very tough, transparent coating formed in several minutes. Since plioform is a thermosetting plastic, hot-air blasts should not be used to accelerate the drying of the coating. Plioform is resistant to HCl, H<sub>2</sub>SO<sub>4</sub>, weak acids, alkalies, alcohols, and ketones. A more complete résumé of its rather amazing properties may be found in the Handbook of Chemistry and Physics 25/. Smith and Pingel 27/ used a plastic coating composed of 9% ethyl cellulose, 18% petroleum naphtha, 55% toluol, and 18% ethyl alcohol in their investigation of 24-S aluminum alloys. The plioform coating performed so well under the experimental conditions imposed upon it that the ethyl cellulose plastic was not used. The plioform coating was so tenacious that when some specimens were reduced 15% in thickness by rolling, the film elongated with the grains to cover the same area that was covered in the original specimen. The plastic coating also protected the freshly polished and etched surface from oxidation by the atmosphere.

Experimental Technique. A pinhole through the plastic coating near the center of each grain was made with a fine needle while the operator observed the metal surface and pin through the microscope. A glass capillary tube filled with 1 Normal KCl was then placed over the pinhole and solution was allowed to fill the hole. Glass capillary tubes were made in the laboratory from standard glass tubing (1/8-in. outside diameter) by drawing over a Bunsen burner. The outside diameter of the capillary tubes varied from 0.005 to 0.02 in. The smaller diameter capillary tubes were the more desirable, as they allowed complete control of the flow of solution over the surface of the metal. The plastic coating helped to restrict the flow of solution over the surface and insured that the potential of a selected region within a single grain would be measured.

Electrical Circuit. The electrical circuit containing the unknown potentials of the nickel grains included the calomel half-cell, salt-bridge, capillary tube, and the nickel metal. Copper wires from the calomel half-cell and the underside of the nickel completed the circuit through the potentiometer. The calomel cell was constructed according to directions given in Daniels 11/. The calomel reference electrode has a temperature coefficient of  $-2.4 \times 10^{-4}$  volts/deg C. In this experimental work any potential change due to changes in temperature of the cell was neglected. A wiring diagram (Figure 1) of the potentiometer circuit is shown on page 11.

Microscope Magnifications Used. Magnifications of 35 and 70 diameters were used to investigate the cast nickel samples; magnifications of 150 and 300 diameters were used in working with the electrolytic nickel sheet and the wrought nickel bars.

Experimental Results. The potential of each grain was measured twice, and it was found that the results were reproducible within plus or minus 5 millivolts. The potentiometer is capable of measuring voltages to 5 significant figures, but as the potentials could not be duplicated beyond the third decimal place, such measurements were not made. Photographs of the experimental apparatus are shown in Figure 2, page 12, and Figure 3, page 13.

Sketches or photographs of the samples studied with the potentials in millivolts given on each grain measured are presented on the pages following the photographs of the equipment. The potential measurements are also tabulated on the pages following each sketch.



CIRCUIT DIAGRAM

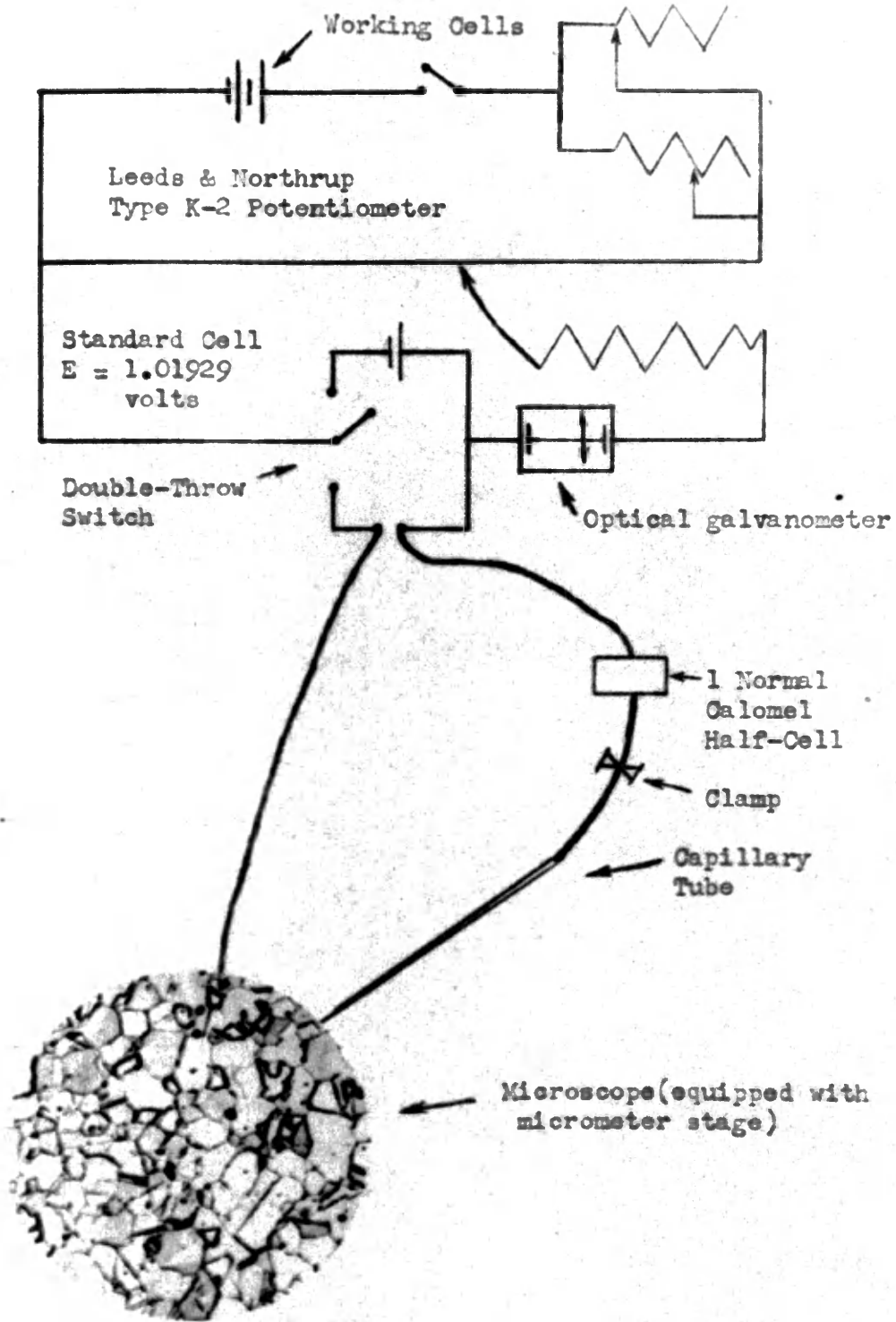


Figure 1

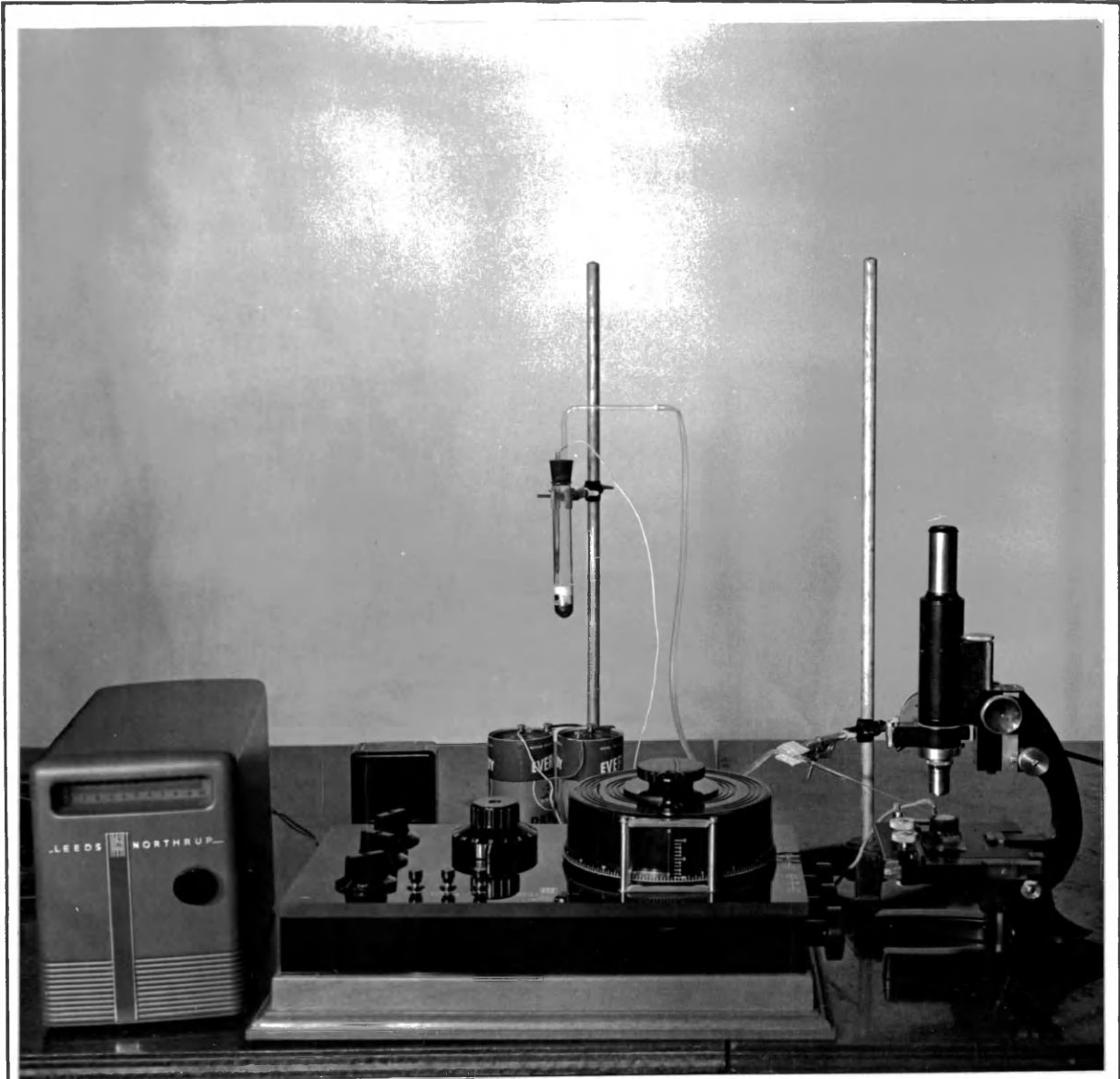


Figure 2: Photograph of Experimental Apparatus

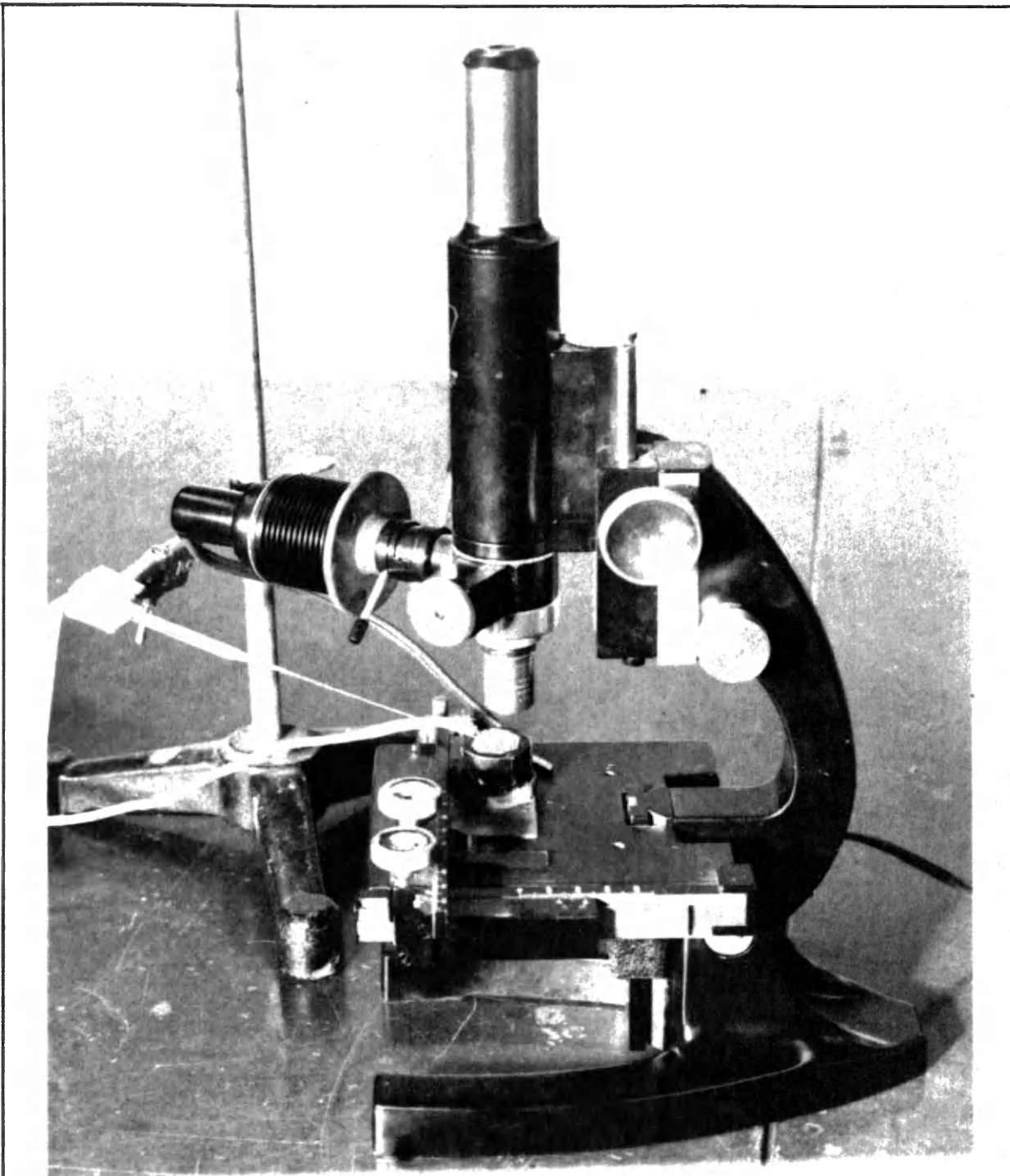


Figure 3: Photograph of specimen (mounted in bakelite) in place on the microscope stage.



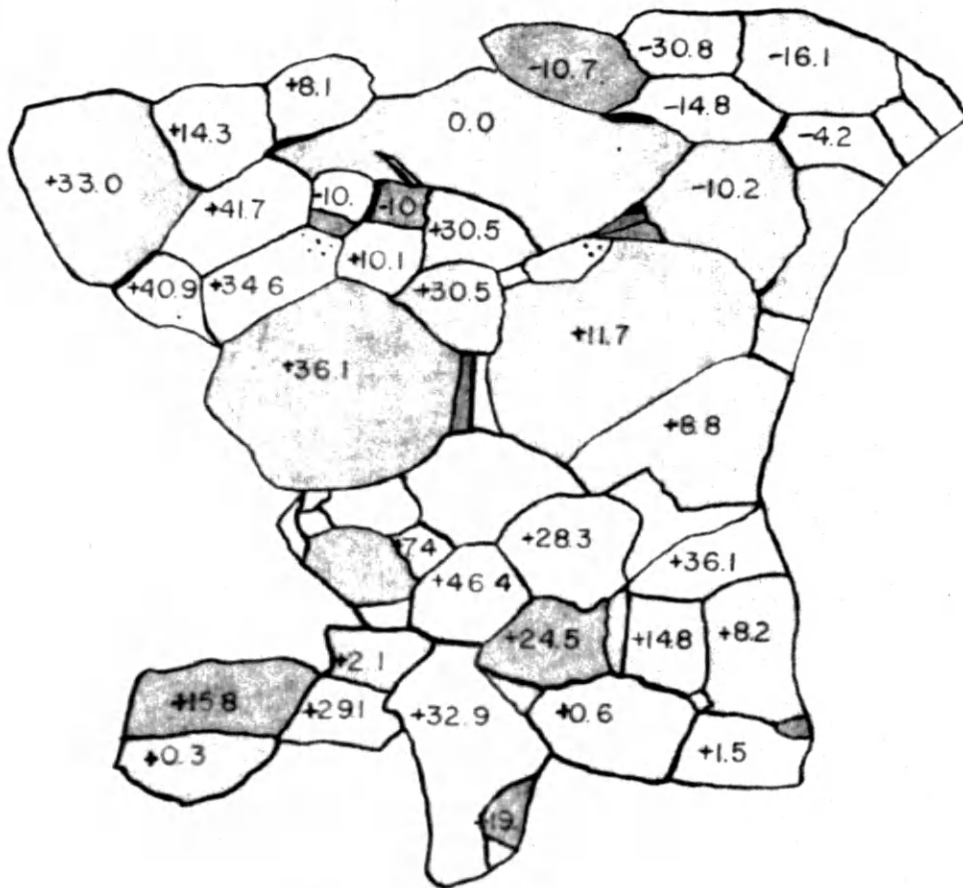
Figure 4: Photograph of cast nickel ingot melted in an induction furnace. Magnification: 5X.

Cast Nickel Metal (commercially pure)

Sodium cyanide-ammonium persulphate etch

Magnification: 70X

The potential of each grain is given in millivolts relative to the potential of the grain marked 0.0



## Potential Measurements of Cast Nickel Section (millivolts\*)

1.	0	21.	28
2.	8	22.	7
3.	14	23.	46
4.	33	24.	36
5.	-11	25.	8
6.	-31	26.	15
7.	-16	27.	1
8.	-15	28.	1
9.	-4	29.	19
10.	42	30.	33
11.	-10	31.	2
12.	-10	32.	29
13.	30	33.	16
14.	10	34.	0
15.	41	35.	36
16.	35	36.	24
17.	30	37.	-10
18.	-10		
19.	12		
20.	9		

The maximum potential difference between grains recorded during the experiment was 77 millivolts.

This specimen was cast from a wrought nickel bar re-melted in a high frequency induction furnace. After the melting, the nickel was allowed to solidify and cool to room temperature in the mold. The resulting ingot was very soft, having a hardness just below 0 on the Rockwell B scale.

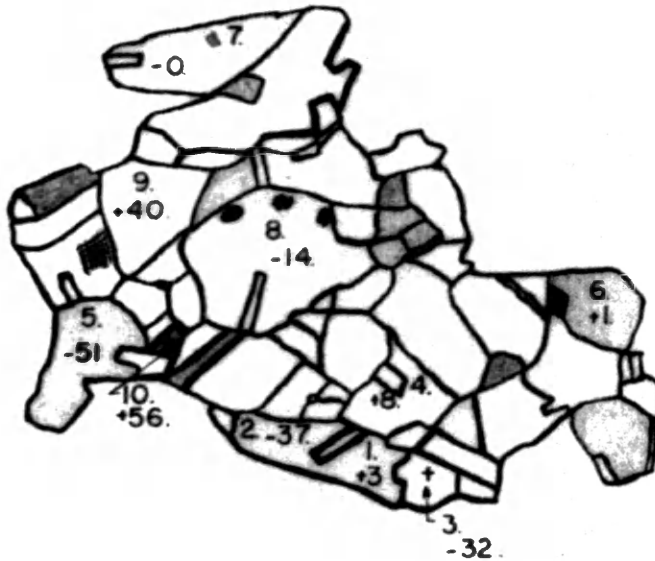
\* In order to emphasize the potential differences existing on the specimen, the potential of each grain has been rounded off to the nearest millivolt and compared with the potential of the grain labeled 0.0. The actual emf of Grain No. 0.0 is 0.21220 absolute volts anodic to a 1 Normal calomel reference electrode.

Annealed Electrolytic Nickel Sheet

Magnification: 150X  
Cyanide-Persulphate etch  
Vertical Illumination

Potential Measurements in millivolts

Maximum Potential Difference: 107 millivolts



## Potential Measurements of Electrolytic Nickel Sample (millivolts\*)

1.	3
2.	-37
3.	-32
4.	8
5.	-51
6.	1
7.	0
8.	-14
9.	40
10.	56

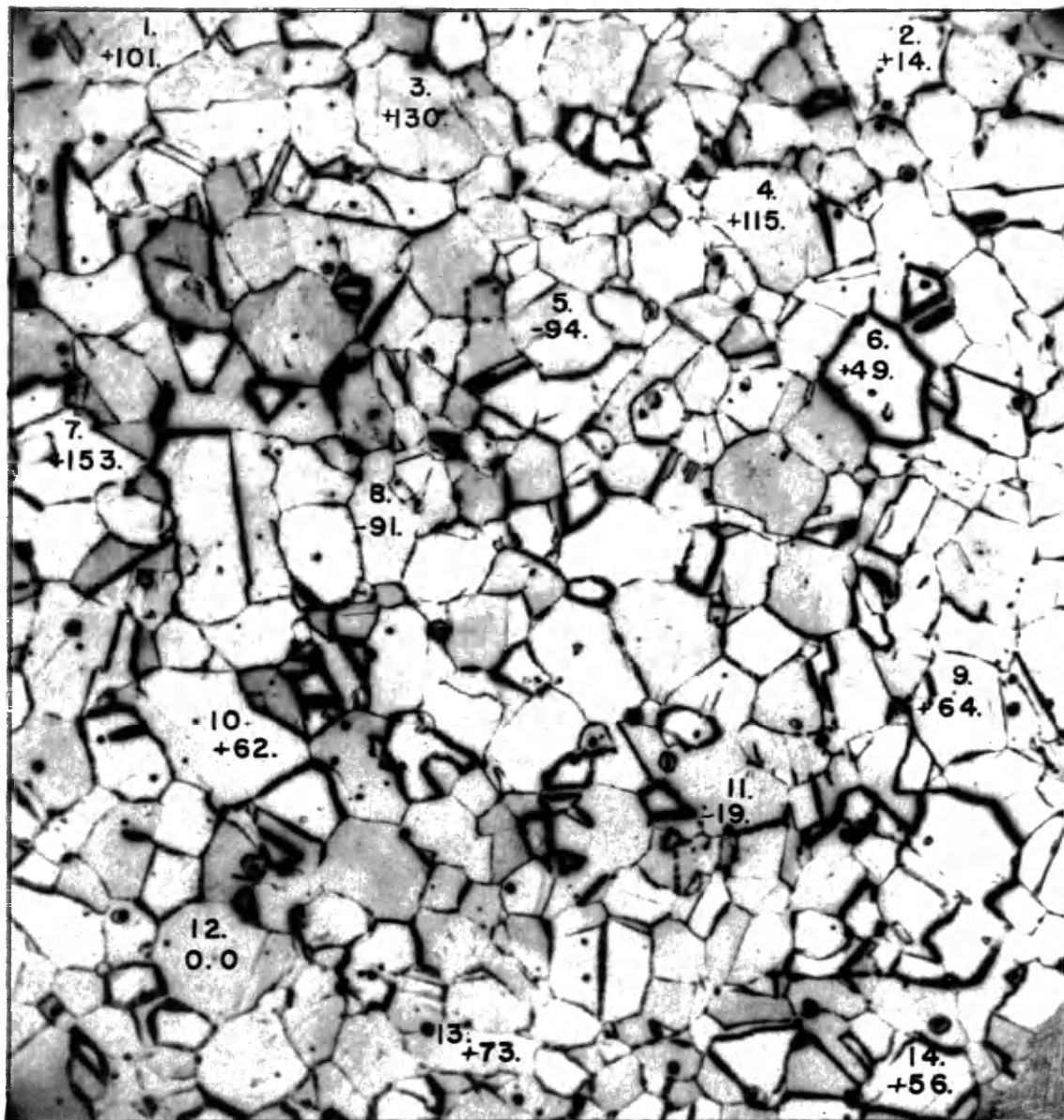
The maximum measured potential difference was 107 millivolts.

The specimen had a hardness of Rockwell<sub>B</sub> 7.

The electrolytic nickel sheet was annealed at 1700 deg F before polishing and etching.

\* The potential of Grain No. 7 is 0.26076 absolute volts anodic to a 1 Normal calomel half-cell.





Wrought Nickel Rod

Cyanide-persulphate etch  
Magnification: 400X

Potential measurements in millivolts

Maximum potential difference observed was 247 millivolts

Potential Measurements on Wrought Nickel Rod (unannealed)

Readings are given in millivolts. \*

1.	101
2.	14
3.	130
4.	115
5.	-94
6.	49
7.	153
8.	-91
9.	64
10.	62
11.	-19
12.	0
13.	73
14.	56

The maximum observed potential difference was 247 millivolts.

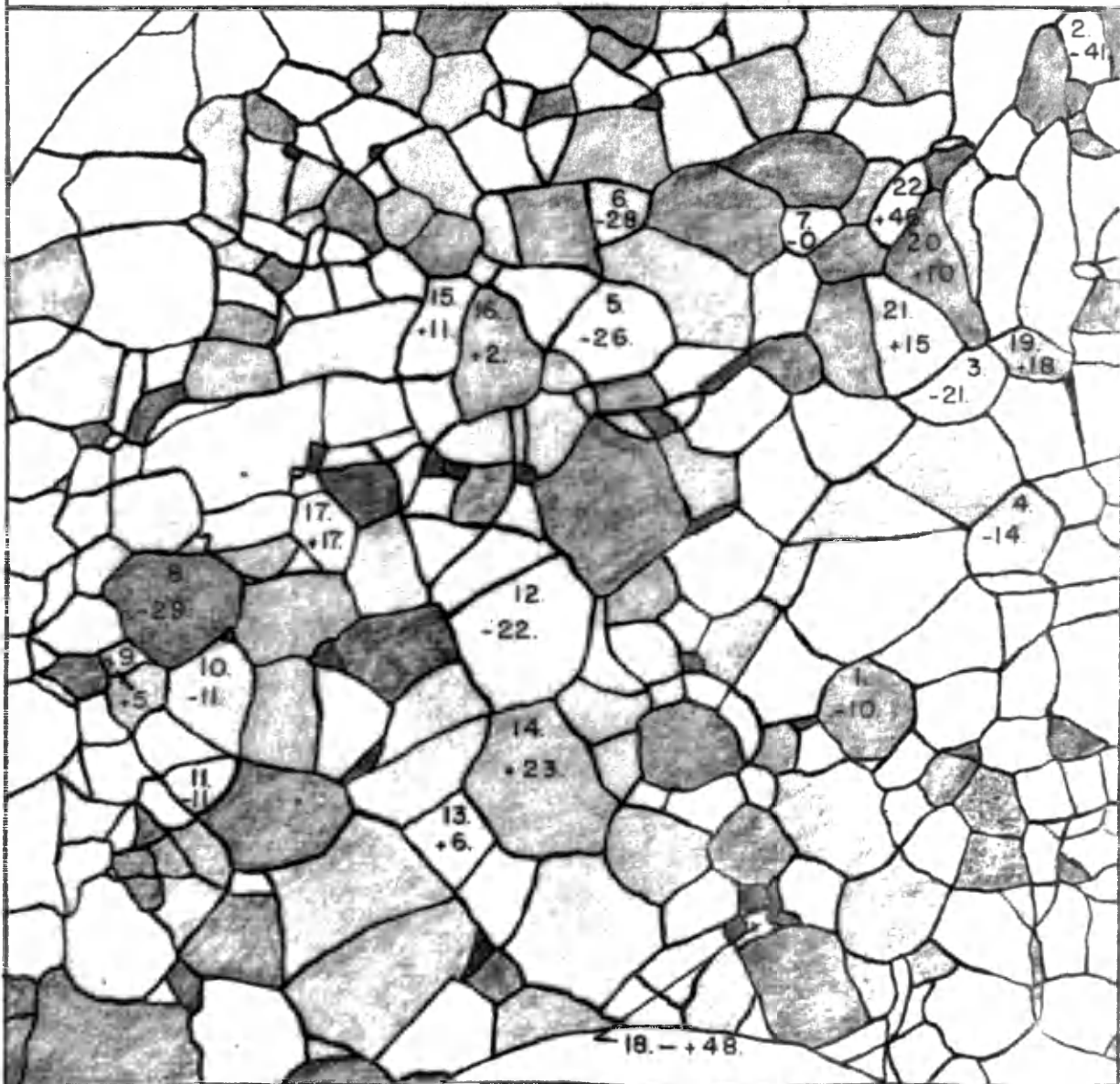
The sample had a hardness of Rockwell<sub>B</sub> 94.

\* The potential of Grain No. 12 is 0.1000 absolute volts relative to a 1 Normal calomel electrode.

Section through Nickel Ingot --  
-- Before 15% reduction in width by rolling

Magnification: 35X  
Cyanide-Persulphate etch  
Vertical Illumination

Potential measurements in millivolts



## Potential Measurements of Cast Nickel Section (millivolts \*)

No.	Before Rolling	After Rolling	Notes
1.	-10	-32	-
2.	-41	-38	Many slip bands in grain.
3.	-21	-16	Many slip bands in grain.
4.	-14	-20	Many slip bands in grain.
5.	-26	1	-
6.	-28	-33	Many slip bands in grain.
7.	0	-8	Many slip bands in grain.
8.	-29	-4	Few slip bands in grain.
9.	5	lost	-
10.	-11	-3	Many slip bands in grain.
11.	-11	6	Many slip bands in grain.
12.	-22	-24	Many slip bands in grain.
13.	6	11	Many slip bands in grain.
14.	23	-13	-
15.	11	-10	-
16.	2	-10	Many slip bands in grain.
17.	17	-3	Few slip bands in grain.
18.	48	42	-
19.	18	-141	No slip bands.
20.	10	-72	Few slip bands in grain.
21.	15	-37	Few slip bands in grain.
22.	46	-9	Few slip bands in grain.

The maximum observed potential difference before rolling was 89 millivolts; the maximum difference after rolling was 183 millivolts.

The hardness of the sample changed from Rockwell<sub>B</sub> 1 to Rockwell<sub>B</sub> 45.

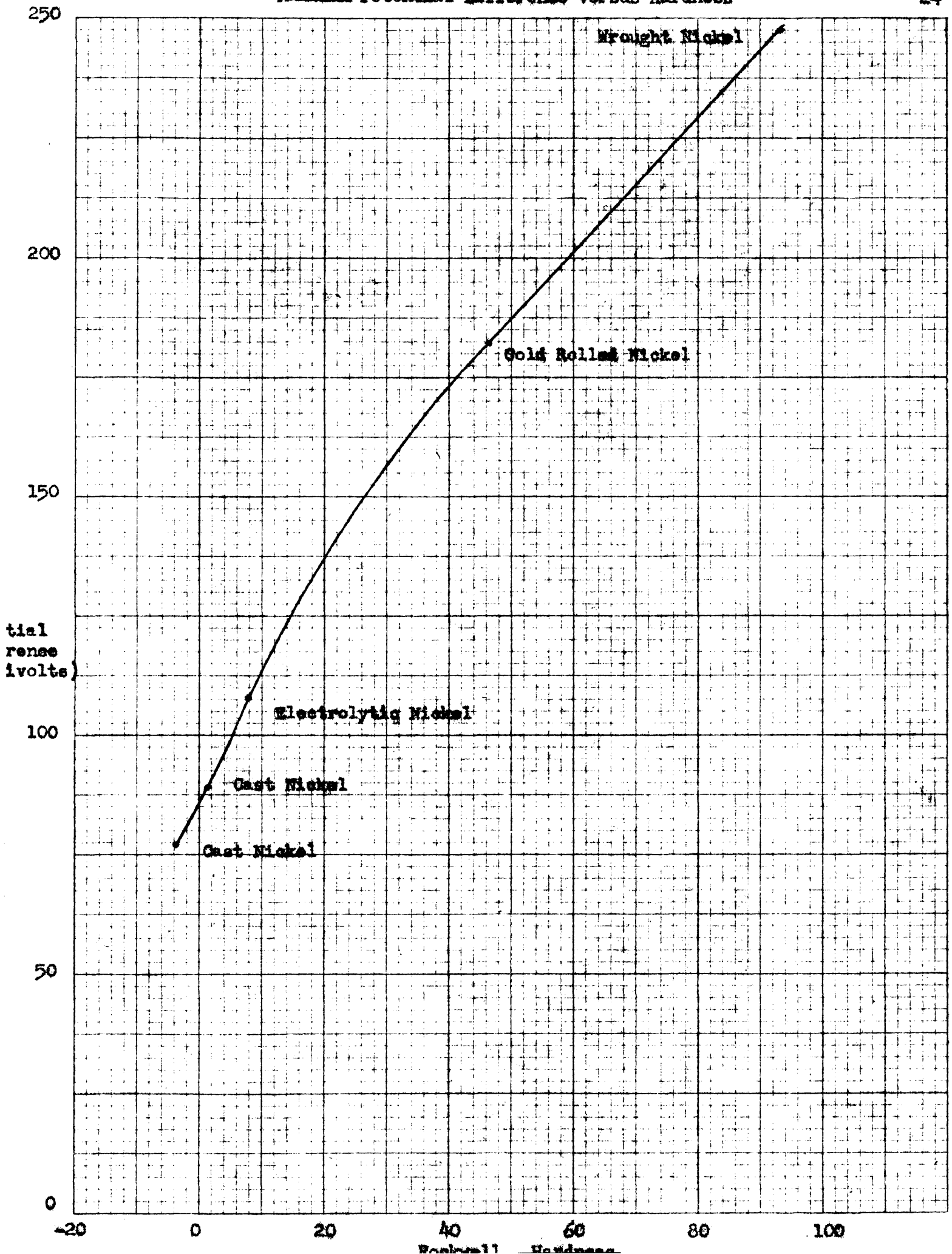
\* The actual potential of Grain No. 7 before rolling is 0.24137 absolute volts anodic to the calomel reference electrode.

An interesting correlation was observed between the measured hardness of the sample and the maximum potential differences existing between the grains. The graph of hardness versus potential differences gives a smooth curve which is shown on the following page.

It is postulated that hardness may be used to evaluate the free energy condition existing on the surface of the metal. The hardness values used are an average of three individual measurements.

<u>Sample</u>	<u>Hardness Rockwell B</u>	<u>Maximum Individual Difference*</u>
Ingot (as cast)	- 4	77
Ingot (as cast)	1	89
Ingot (cold rolled)	45	183
Electrolytic sheet	7	107
Wrought nickel rod	94	247

\* Maximum Individual Difference given in millivolts.

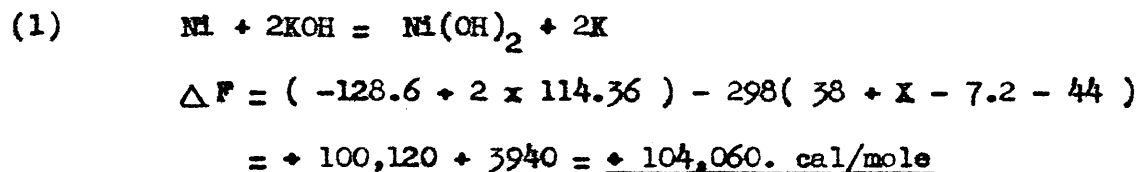


### Thermodynamic Considerations

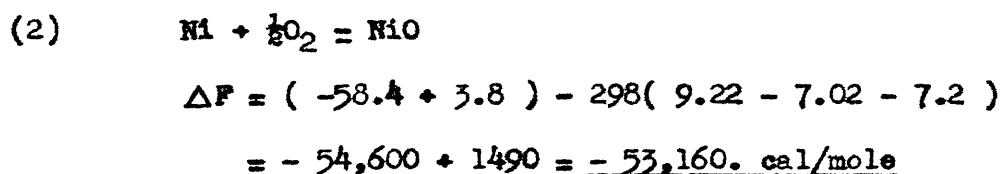
The electrochemical corrosion of nickel may proceed in any of several ways depending on the corroding media, surrounding atmosphere, and the condition of the metal surface. However, the general tendency of nickel to corrode in any given environment can be predicted from thermodynamic calculations based on the energy equation:

$\Delta F = \Delta H - T(\Delta S)$  where  $\Delta F$  is the free energy change,  $\Delta H$  is the total enthalpy of reaction,  $T$  is the absolute temperature in deg K, and  $\Delta S$  is the entropy change.

A negative free energy change as interpreted in the following data indicates the possibility of a spontaneous reaction. The entropy change is relatively insignificant and is included only to improve the technical accuracy of the presentation. Some entropy values are not known and are not included in the calculations.



$\Delta S$  for potassium is not known. The reaction is not spontaneous and nickel should not be expected to corrode in strong hydroxides by this mechanism.

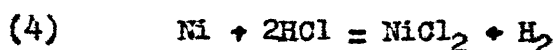


The reaction is spontaneous and nickel could be expected to react with the dissolved oxygen in solutions exposed to air.



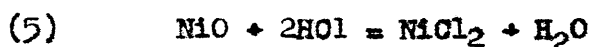
$$\begin{aligned} \Delta F &= ( -128.6 - 86.4 + 58.4 + 200.2 ) - 298( 19 - 9.2 ) \\ &= + 43,600 + 7500 = \underline{+ 51,100 \text{ cal/mole}} \end{aligned}$$

The reaction is not spontaneous but is more probable than (1).



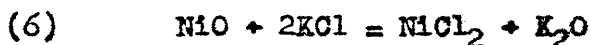
$$\begin{aligned} \Delta F &= ( -93.2 + 80.04 ) - 298( 31.2 - 13.2 - 7.2 ) \\ &= - 13,160 - 3180 = \underline{- 16,340 \text{ cal/mole}} \end{aligned}$$

The calculation indicates that nickel should react with acids.



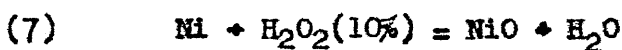
$$\begin{aligned} \Delta F &= ( -93.2 - 68.32 + 58.4 + 80.04 ) - 298( 16.7 - 13.2 - 9.2 ) \\ &= - 23,080 + 1700 = \underline{- 21,380 \text{ cal/mole}} \end{aligned}$$

Any nickel oxide film on the nickel should be destroyed by an acid such as HCl.



$$\begin{aligned} \Delta F &= ( -93.2 - 86.4 + 200.2 + 58.4 ) - 298( X ) \\ &= \underline{+ 79,000 \text{ cal/mole}} \end{aligned}$$

Nickel coated with nickel oxide should not corrode in neutral salt solutions.



$$\begin{aligned} \Delta F &= ( -58.4 - 68.32 + 45.66 ) - 298( 9.22 - 7.2 ) \\ &= - 81,060 - 600 = \underline{- 81,660 \text{ cal/mole}} \end{aligned}$$

The calculation indicates a definite tendency for nickel to form nickel oxide in an oxidizing medium.

The thermodynamic values for free energy, enthalpy, and entropy were taken from Circular #500 published by the National Bureau of Standards 56/.



It must be remembered that thermodynamic calculations of the type shown above do not predict the time required for a reaction to go to completion but show merely that a reaction is or is not possible. It has been found that nickel reacts slowly to form NiO and that nickel may become passive in mediums which should corrode it.

$$\Delta F = - nFE \text{ where: } E \text{ is the potential in volts}$$

$$F \text{ is } 23,060 \text{ calories/volt or } 96,500 \text{ coulombs}$$

$$n \text{ is the valence change}$$

$$\Delta F \text{ is the free energy change}$$

Temperature and pressure are assumed constant.

The maximum potential difference existing between grains on the surface of the cast nickel metal was approximately 80 millivolts.

$$\Delta F = - 2 \times 23,060(0.080) = \underline{- 3690 \text{ cal/mole}}$$

The maximum potential difference measured on the wrought nickel rod was 247 millivolts.

$$\Delta F = - 2 \times 23,060(0.247) = \underline{- 11,400 \text{ cal/mole}}$$

The liquid junction potential may be rendered nearly negligible by using a salt bridge of potassium chloride 11/.

### Conclusions

The potential measurements show that potential differences do exist between grains on the surface of nickel metal. These potential differences are greater for cold-worked materials than for metal in an as-cast condition. Small grains tend to be anodic to larger adjacent grains, but factors other than size may outweigh this consideration.

The photograph of the wrought nickel bar shows clearly that some of the grain boundaries have been etched more and are therefore more anodic than others. In general the grain boundaries are etched more than

the grains, demonstrating that the boundaries are anodic to the grains. Aust and Chalmers 3/ state that the grain boundary energy is controlled by the relative orientations of the crystals adjacent to the boundary. It seems reasonable to assume that these boundaries have higher energies than do the grains. Certain boundaries have been observed to etch very rapidly. These boundaries appear as wide black lines in the sketches and photographs. We might consider that the grains adjacent to these boundaries have assumed orientations such that there is a large free energy difference between them.

The energy present on the surface of a metal represented by potential differences will accelerate reactions and may be high enough in some cases to instigate new reactions whereby corrosion may proceed.

Slip furnishes a means whereby metals may reduce the amount of free energy retained in the grains. As some metals are deformed more easily than others and slip along certain crystallographic planes more readily, the adverse effects of cold work will vary from metal to metal. An interesting correlation of hardness with the measured potential differences was observed.

Potential measurements qualitatively indicate why corrosion is more rapid on some specimens than on others. Current measurements are necessary to predict the actual corrosion rates 23/, 28/, 29/, 49/, and 55/.

Potential measurements do not directly explain the passivity of nickel in some acids; but as the Ni/NiO cell and the NiO films are being investigated currently by several research teams, it may be found that the potential differences are minimized when a thick film of NiO forms.

In the author's opinion, the formation of NiO is the first step in the corrosion of nickel and may or may not be a "protective film" to stifle further corrosion.

It appears that if a metal could be prepared in such a manner as to develop a preferred orientation of the least active planes near the surface and to contain homogeneous grains of approximately equal size, then a truly corrosion-resistant material would be available for use.

## SPECTROGRAPHIC DETERMINATIONS

### Introduction

Spectrographic techniques were employed to determine the impurities present in the nickel, the location of these impurities, and the manner in which the impurities were present ( i.e. solid solution, compound, or element ). The manner in which the impurities are retained should affect the potentials between the grains and the boundaries, between different grains, and within the individual grains if the grains are not homogeneous. The location of the impurities in the nickel should have an important bearing on the corrosion resistance of nickel in various media and should also help to explain why nickel is occasionally subjected to severe intergranular corrosion.

### D-C Arc Analysis

Nominal composition of electrolytic nickel: 45/

Ni + Co = 99.95% minimum  
0.05% total impurities

Nominal composition of wrought nickel: 46/

Ni + Co = 99.4%  
Cu = 0.10%  
Fe = 0.15%  
Mn = 0.20%  
Si = 0.05%  
O = 0.10%  
S = 0.005%

A Baird 3-meter grating spectrograph was used for this analysis, with an ARL rectifier unit supplying 6 amperes d-c to the arc. An ARL comparator-densitometer was used to interpret the results obtained.

Excitation Data:

Range: 2250-3600 Angstroms  
 Emulsion: III-0  
 Development: D-19 for 5 minutes  
 Slit width: 25 microns  
 Line mask: 4 millimeters  
 Arc gap: 5 millimeters  
 Current: 6 amperes  
 Exposure: 20 seconds

Fifty-milligram samples of electrolytic nickel and 50 milligrams of wrought nickel were volatilized from 5-millimeter craters drilled in  $\frac{1}{4}$ -inch carbon rods. Three-sixteenths-inch carbon cathodes were used as the counter electrodes. Although the electrolytic nickel contained a smaller quantitative amount of each impurity than did the wrought nickel, the same metallic impurities were present in both. In the following discussion no distinction will be made between the two types.

Four analyses of the metal were made on different days to determine the impurities present.

The relative intensities of the lines were visually estimated and then after the absolute intensity of the line under examination as given by Brode 5/ had been considered, the elements present were assigned to 4 groups.

- (1) S: Strong, the element was present in large quantities, 1-100%. The lines were very dense, all lines were present, the strongest lines had undergone a reversal on the plate.

- (2) M: Minor, the element was present in small quantities, approximately 0.05-1.0%. The lines were black and almost all of the lines for the element were present. No line reversal had taken place.
- (3) T: Trace, the element was present as a trace impurity. The lines were clearly resolved. Only the persistent lines were present and they had a medium intensity.
- (4) FT: Faint trace, the element was present as a very faint trace. The lines were very weak and only 2-3 persistent lines were present. The element was present above the lower detection limit of the spectrographic method used.

Nickel Analysis:

Major constituent:  
nickel

Minor impurities:  
cobalt  
iron  
manganese  
silicon  
titanium

Trace impurities:  
aluminum  
antimony  
carbon (detected using copper electrodes)  
chromium  
copper  
magnesium  
phosphorus  
lead  
silver  
tungsten  
zinc

Although oxygen and sulphur are not detectable by the method used, they were probably present in small amounts 46/.

### A-C Spark Analysis

Special a-c spark methods (microarea analysis) were used to analyze the grain boundaries and the grains to determine the relative amounts of contaminating elements present in each. A Baird 3-meter grating spectrograph and an ARL spark source were used for the investigations.

For this investigation, a 75-gram cast ingot was prepared from a wrought nickel bar by induction melting. The sample, after very slow cooling in the mold, was polished and then etched with sodium cyanide and ammonium persulphate to bring out the grains and grain boundaries.

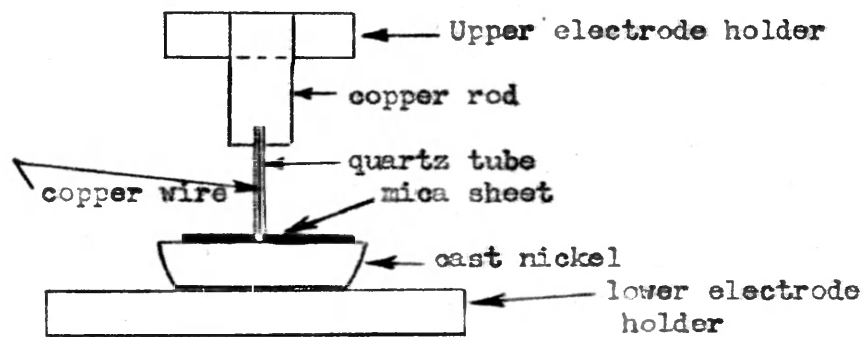
A copper wire (0.01-inch diameter) was placed inside a quartz capillary tube (0.06-inch outside diameter). This tube and wire were cemented into a 1/16-inch hole drilled in a 1/4-inch copper rod. The copper rod was then placed in the electrode holder.

A mica sheet, 3 to 5 millimeters thick, with a very small hole (0.01-inch diameter) was placed over the area of the nickel to be investigated. While the sheet and the surface of the metal were under observation through a microscope at 100X magnification, the sheet was moved over the metal until the hole exposed either a grain boundary or a grain center as desired.

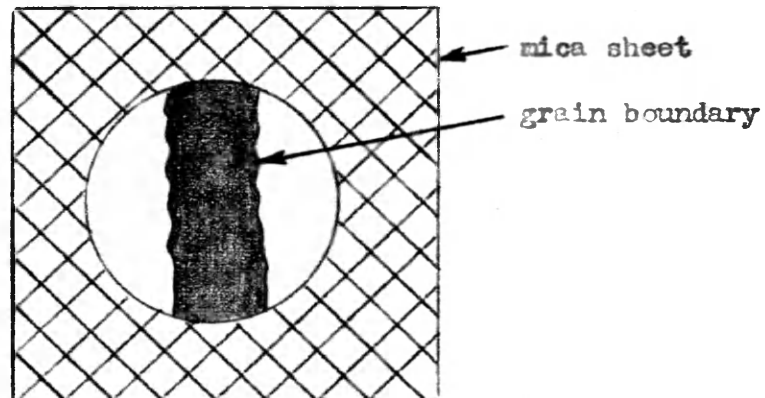
#### Excitation Data:

Range: 2250-3600 Angstroms  
Emulsion: 103-a0  
Development: D-19 for 5 minutes  
Slit width: 25 microns  
Line mask: 4 millimeters  
Arc gap: 4 millimeters  
Exposure: 20 seconds  
Volt-amperes: 2/3 KVA  
Inductance: 2  
Rotary gap: 4

The spark was directed from the tube to the exposed metal area. The behavior of the spark resembled that of a d-c arc in that it did not wander but remained as a straight line when focused on the slit. The steady spark made it possible to use a finer slit and a shorter exposure time than had been anticipated.



Sketch of apparatus



View of area under examination (1000X)

Glass capillary tubes were tried, but they were not strong enough to resist the dielectric shocks imposed by the a-c spark. The copper wire would burn back very slowly in the quartz tube until the spark refused to jump the gap. The quartz tube was then broken back and the electrode used again. The hole in the mica sheet did not enlarge unless the spark gap increased beyond 5 millimeters.



A d-c arc and a Hartman diaphragm were used to analyze the mica, the copper wire, the quartz tube, and the carbon rods to determine the impurities present in them so that in subsequent analyses these elements would not be credited as impurities in the nickel. The excitation conditions were the same as described in the preceding section on the d-c arc except that Spectrum Analysis No. 1 film was used.

Copper Wire Analysis:

Major constituent  
copper

Minor impurities  
magnesium

Trace impurities  
aluminum  
iron (FT)  
lead (FT)  
nickel (FT)  
silicon (FT)  
silver

Quartz Tube Analysis:

Major constituent  
silicon

Minor impurities  
none

Trace impurities  
antimony (FT)  
calcium  
copper  
iron (FT)  
magnesium  
manganese (FT)  
lead (FT)

Carbon Rod Analysis:

Major constituent  
carbon

Trace impurities  
cobalt (FT)  
magnesium (FT)  
silicon (FT)

**Mica Analysis:**

**Major constituent**  
silicon

**Trace impurities**  
aluminum  
calcium  
copper  
iron  
magnesium  
silver (PT)  
sodium

When interpreting the results obtained, any spectrum in which the nickel lines appeared weak, was considered to consist primarily of the material from the grain boundary. When the nickel lines appeared strong, the grains were considered responsible for the spectrum obtained. It should be kept in mind that all exposures were for the same length of time.

Tabulation of Experimental Results

Sample	Element																		
	.Ag.	.Al.	.C	.Ca.	.Oo.	.Cr.	.Cu.	.Fe.	.Mg.	.Mn.	.Ni.	.P	.Pb.	.Sb.	.Si.	.Ti.	.W	.Zn.	
d-c arc																			
50 mg Nickel	T	T	T	-	M	T	T	M	T	M	S	T	T	FT	M	M	T	T	
Copper Wire	T	T	-	-	-	-	S	FT	M	-	FT	-	FT	-	FT	-	-	-	-
d-c arc																			
Quartz Tube	-	-	-	T	-	-	T	FT	T	FT	-	-	FT	FT	S	-	-	-	-
d-c arc																			
Carbon Rods	-	-	S	-	FT	-	-	FT	-	-	-	-	-	-	FT	-	-	-	-
d-c arc																			
Mica sheet	FT	T	-	T	-	-	T	T	T	-	-	-	-	-	S	-	-	-	-
d-c arc																			
a-c spark to Nickel Grains	T	T	T	T	M	-	S	M	T	M	S	T	T	FT	M	M	T	T	T
	T	T	T	T	M	-	S	M	T	M	S	T	T	-	M	M	T	T	T
	T	T	T	T	M	T	S	M	T	M	S	-	T	-	M	M	T	T	T
	T	T	T	T	T	T	S	M	T	M	S	T	T	T	S	M	T	T	T
	T	T	T	T	M	T	S	M	T	M	S	T	T	T	S	M	T	T	T
	T	T	T	T	T	T	S	M	T	M	S	T	T	T	S	M	T	T	T
	T	T	T	-	T	T	S	M	T	M	S	T	T	T	S	M	T	T	T
a-c spark to Grain Boundaries	-	T	T	-	-	-	S	M	T	-	T	-	-	FT	M	T	-	-	-
	T	-	T	-	-	-	S	M	T	-	T	-	-	FT	M	T	-	-	-
	T	T	T	-	-	-	S	M	T	M	M	-	-	FT	M	T	-	-	-
	T	T	T	-	-	-	S	M	T	-	M	-	-	FT	M	T	-	-	-
	T	T	T	T	FT	-	S	M	T	T	M	-	-	FT	M	T	-	T	-
	T	FT	T	T	-	-	S	M	T	-	T	-	T	FT	M	T	FT	-	-
	T	T	T	T	-	-	S	M	T	T	T	FT	T	FT	M	T	-	-	-
	T	T	T	T	-	-	S	M	T	T	T	-	-	T	M	T	-	T	-

S = strong, major constituent  
 M = minor amount  
 T = trace amount  
 FT = faint trace present

Relative Solubility of Detected Impurities in Nickel Metal

1. Ag(silver) - Approximately 3% silver soluble in solid solution 45/.
2. Aluminum - 5% aluminum in solid solution at 700 deg C 45/.
3. Carbon - 0.03% carbon soluble at 500 deg C.
4. Calcium - Not present in nickel metal.
5. Cobalt - Completely soluble in all proportions 45/.
6. Chromium - Completely soluble 45/.
7. Copper - Completely soluble 45/.
8. Fe(iron) - Completely soluble 45/.
9. Magnesium - -0.10% soluble at 1100 deg C 45/.  
Forms intermetallic compound, MgNi<sub>2</sub>, 32/.
10. Manganese - Forms a solid solution 45/.
11. Oxygen - 0.02% soluble at 600 deg C 45/.
12. Phosphorus - Forms an intermetallic compound, Ni<sub>3</sub>P, 32/.
13. Pb(lead) - Approximately 2% soluble 54/.
14. Sulphur - 0.005% soluble 45/.
15. Sb(antimony) - slightly soluble, forms an intermetallic  
compound, NiSb, 32/.
16. Silicon - Forms solid solution with nickel 45/.
17. Titanium - Forms solid solution with nickel 45/.
18. Tungsten - Forms solid solution with nickel 45/.
19. Zinc - Forms solid solution with nickel 45/.

Interpretation of Data

Element	Detection Limit	Line Intensity	%Element Present	Remarks
Ag	0.00005%	1000	Trace	Silver present in solid solution. Because of high sensitivity, method is unable to place location of silver.
Al	0.0002%	800-1000	Trace	In wrought Ni, Al is present in grains and boundaries.
C	-	-	0.10%	C is present in grains and in grain boundaries.
Ca	0.002%	300	-	Ca is present from the mica and the quartz.
Co	0.001%	150	99.4 Ni and Co	Co present in nickel metal.
Cr	0.0001%	400	Trace	Cr present in nickel metal.
Cu	0.00005%	2000	0.10	A comparison of relative intensities of Cu lines shows Cu present in metal, not boundaries.
Fe	0.0005%	600	0.15%	Iron is present in the grains and in the boundaries.
Mg	0.0002%	300	Trace	Mg is present in the grains and the grain boundaries.
Ni	0.0005%	100	99.4%	
P	0.0005%	100	Trace	
Pb	0.0005%	100	Trace	Present in solution with nickel.
Sb	0.002%	200	Trace	Present in grains and in boundaries.
Si	0.002%	300	0.05	Present in the grains.
Ti	0.001%	300	Minor	Present in grains.
W	0.002%	25	Trace	Present in the grains.
Zn	0.01%	800	Trace	Present in the grains.
O	-	-	-	Present in wrought nickel as oxides.
S	-	-	-	Present in wrought nickel as stable sulphides.

## Conclusions

Aluminum, antimony, carbon, cobalt, chromium, copper, iron, magnesium, nickel phosphide ( $\text{Ni}_3\text{P}$ ), lead, silicon, silver, titanium, tungsten, and zinc are present in the nickel grains.

Aluminum, antimony, carbon, iron, magnesium, and nickel are present in the grain boundaries as carbides, oxides, and sulphides.

The nickel grains are homogeneous with very few inclusions. The grain boundaries contain very little material (quantitatively) and are composed of stable compounds. Only when the nickel is exposed to conditions which will selectively dissolve the stable oxides of nickel, aluminum, iron, carbides, and sulphides will nickel metal be subjected to severe intergranular corrosion.

The homogeneity of the metal will reduce the possibility of local cell formation and will lower the potential differences existing between the grains, within the grains, and between the grains and their boundaries.

Nickel, although comparatively impure, might be regarded as a very effective solvent for the impurities occurring with it and therefore holds the impurities in a form such that they cannot aid in the electrolytic corrosion of nickel. The "effective purity" of nickel closely approximates 100%.

Electrolytic nickel should resist corrosion even more effectively than does the ordinary wrought metal because of the smaller amount of metallic impurities and the almost complete absence of carbides, oxides, phosphides, and sulphides. Although electrolytic nickel is available only in sheets, wrought nickel is available in a variety of forms.

## X-RAY DIFFRACTION STUDIES

### Introduction

X-ray diffraction investigations were undertaken to determine the nature of the corrosion products formed on the surface of nickel metal exposed to various corrosive media. An analysis of the corrosion products formed on the surface of the nickel should help either to verify the conclusion drawn after the spectrographic determination that the impurities in nickel do not accelerate its corrosion or leave this belief open to grave doubt. If compounds of iron, copper, silicon, manganese, carbon, cobalt, etc. are found in the film on the surface, the conclusion may be drawn that these impurities impair the corrosion resistance of nickel. Although electron diffraction equipment is usually employed to study films, X-ray diffraction apparatus has been used with excellent results 27/.

### Technique

A General Electric X-ray diffraction unit was used for the film studies.

An oscillating-crystal technique was used to rotate the sample back and forth through an oblique angle of 0 to 8 degrees in the path of the X-ray beam. The X-ray beam was directed obliquely at the surface of the nickel and then was reflected to photographic film held by normal powder cameras. This method was used so that the beam would strike the corrosion film on the surface of the metal and then

be reflected without penetrating deeply into the metal.

### Experimental Results

#### Excitation Conditions:

Camera: Powder type  
 Film: Kodak No-Screen  
 Development: D-19 for 5 minutes  
 Slit System: Pinhole  
 Target: Copper  
 Primary voltage: 220 volts  
 Secondary voltage: 40 kilovolts  
 Current: 20 milliamperes  
 Filter: Nickel  
 Exposure time: 4 hours

The positions of the diffraction lines on the film were measured to the nearest 0.1 millimeter. The "d" values were determined and compared with known "d" values for various compounds.

(1) The surface of electrolytic nickel sheet which had been exposed to air at room temperatures was investigated.

<u>Line Position</u>	<u>"d" experimental</u>	<u>"d" theoretical</u>	<u>Intensity</u>	<u>Material</u>
1	2.0138 Angstroms	2.01 Angstroms	Strong	Nickel
2	1.7436	1.741	Medium	"
3	1.2354	1.233	Weak	"
4	1.0552	1.053	Weak	"
5	1.0100	1.009	Weak	"

The method was not sensitive enough to detect any NiO, or other compounds if they were present.



(2) The surface of a sheet of electrolytic nickel which had been immersed in nitric acid for two weeks was examined.

<u>Line Position</u>	<u>"d" experimental</u>	<u>"d" theoretical</u>	<u>Intensity</u>	<u>Material</u>
1	2.0735 Angstroms	2.08	Strong	NiO
2	2.021	2.01	Strong	Nickel
3	1.739	1.74	Weak	Ni
4	1.254	1.258	Medium	NiO
5	1.236	1.233	Medium	Ni
6	1.18	1.20	Medium	NiO
7	1.061	1.053	Medium	NiO
8	1.018	1.009	Weak	Ni
9	0.979	0.96	Very weak	NiO

The results indicate that NiO is formed on the surface of nickel exposed to  $\text{HNO}_3$ . The presence of manganese in the film was suspected but could not be conclusively verified.

(3) A sheet of electrolytic nickel was exposed to carbon and air in a furnace at 1700 deg F for 4 hours. The surface of the sample was then examined.

<u>Line Position</u>	<u>"d" experimental</u>	<u>"d" theoretical</u>	<u>Intensity</u>	<u>Material</u>
1	6.45 Angstroms	6.41	Weak	$\text{Ni}_2\text{O}_3$
2	3.31	3.32	Weak	$\text{Ni}_2\text{O}_3$
3	2.49	2.50	Weak	$\text{Ni}_2\text{O}_3$
4	2.40	2.40	Medium	NiO
5	2.08	2.08	Strong	NiO
6	2.017	2.01	Strong	Ni
7	1.753	1.74	Strong	Ni
8	1.71	1.72	Weak	$\text{Ni}(\text{OH})_2$
9	1.53	1.54	Weak	$\text{Ni}(\text{OH})_2$
10	1.468	1.47	Medium	NiO
11	1.407	-	Weak	$\text{Ni}_2\text{O}_3$
12	1.30	1.29	Weak	$\text{Ni}(\text{OH})_2$
13	1.25	1.26	Weak	NiO
14	1.24	1.23	Medium	Ni
15	1.20	1.20	Weak	NiO
16	1.057	1.053	Medium	Ni

The film formed on the nickel sheet exposed to these very corrosive conditions was composed of NiO,  $\text{Ni}_2\text{O}_3$ , and  $\text{Ni}(\text{OH})_2$ .

### Conclusions

When nickel is exposed to corrosive media such as  $\text{HNO}_3$ , or air at high temperatures, a film of NiO formed. If the conditions are severe enough, higher oxides of nickel such as  $\text{Ni}_2\text{O}_3$  will form. The formation of these films probably constitutes the first step in the corrosion of nickel. Nickel immersed in solutions containing dissolved oxygen will probably form NiO as the first step in the corrosion of the metal.

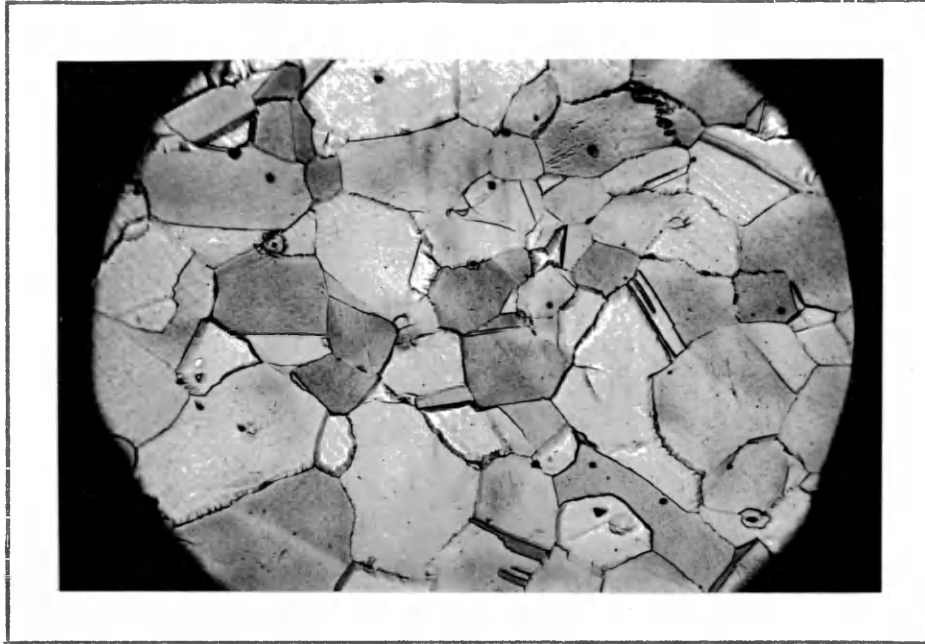
SUPPLEMENTARY METALLOGRAPHIC WORK

During the course of the preceding investigations many additional specimens were prepared and examined. Photographs and data pertaining to these samples are included here in the hope that they will be of interest.



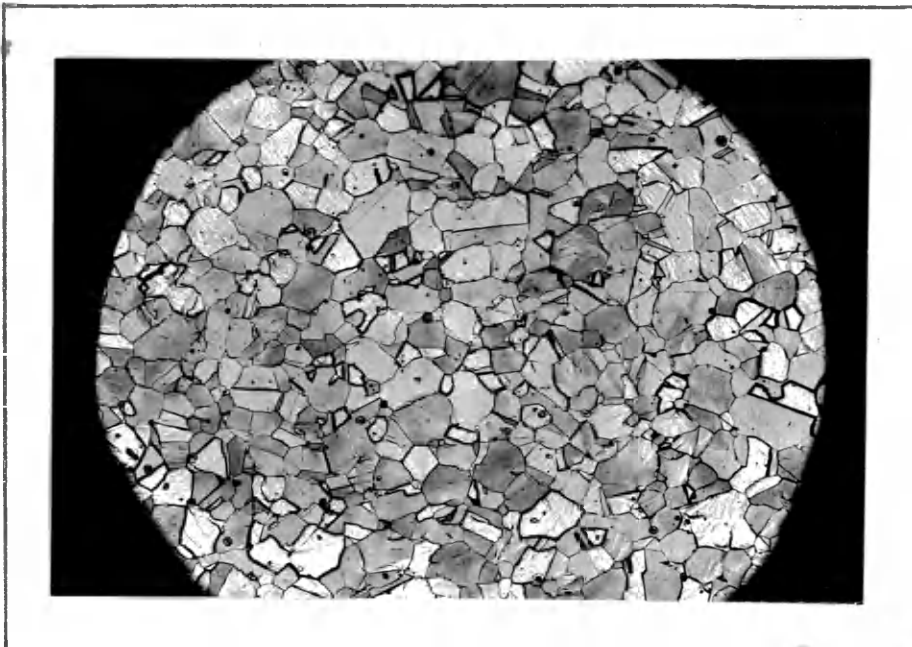
Magnification: 5X  
Cyanide-Persulphate etch for 3 minutes

Photomicrograph of cast nickel ingot in the region where the potential measurements were taken on the cold-rolled sample.



Magnification: 300X  
Cyanide-persulphate etch for 5 minutes

Photograph of wrought nickel bar in region where potential measurements were taken.



Magnification: 100X  
Cyanide-persulphate etch for 5 minutes

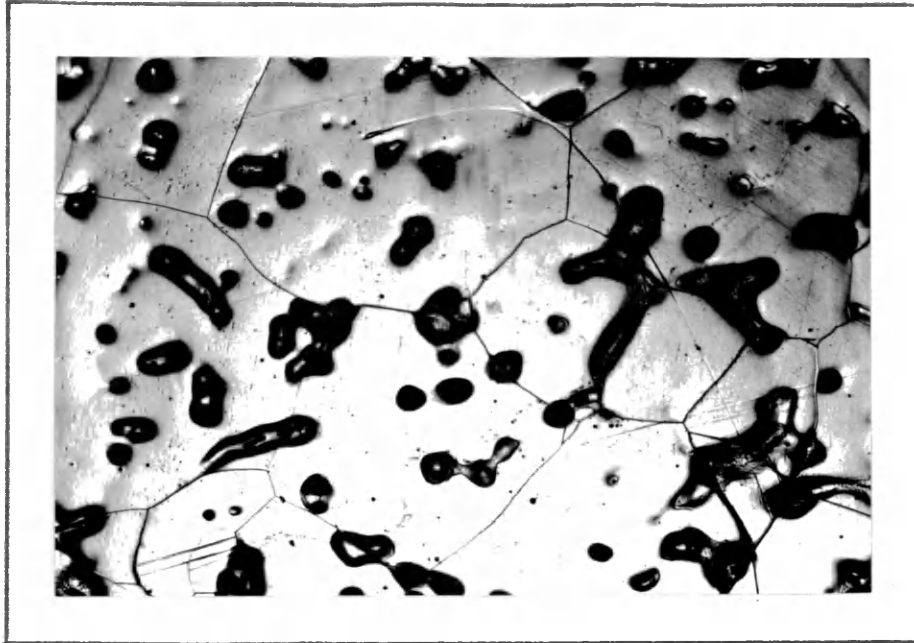
Photograph of wrought nickel bar.

A section of electrolytic nickel sheet was cut into two identical parts. One part was annealed and the other reduced 40% in thickness by rolling. These specimens were then immersed in 10%  $\text{HNO}_3$  together with an annealed nickel casting.



Magnification: 100X  
Etchant: Nitric acid, 10%  
Time: 3 minutes

Photograph of cold-rolled electrolytic nickel sheet. Note geometrical etch pitting.



Magnification: 100X  
Etchant: Nitric acid, 10%  
Time: 3 minutes

Photograph of anealed electrolytic nickel sheet.

The nickel ingot which was immersed in the acid with the cold-rolled specimen and the anealed sample was not attacked by the acid.

An attempt was made to use an indicator similar to the ferroxyll indicator which gives such amazing results on steel. It was intended that the anodic grains would turn gold in color whereas the cathodic grains would turn red. The color changes did not occur as planned. The indicator did etch some groups of grains while leaving the others unattacked.



Magnification: 100X  
Etchant: Ferroxyll indicator containing KCN  
Time: 5 days  
Oblique illumination

### SUMMARY OF CONCLUSIONS

Potential differences varying in magnitude from 0 to 247 millivolts do exist between the grains of commercially pure nickel metal in different forms. These potential differences are caused by crystal orientation differences, size differences, the degree of cold-work, grain boundaries, and other minor factors such as the presence of moisture.

Spectrographic analyses show that the nickel grains are relatively homogeneous and that the boundaries are composed of stable oxides, carbides, and sulphides of aluminum, antimony, carbon, iron, magnesium, and nickel. This homogeneity would minimize any differences in potential resulting from variations in composition.

X-ray diffraction studies disclose that NiO and Ni<sub>2</sub>O<sub>3</sub> are formed on the surface of the nickel metal when it is exposed to oxidizing conditions. The formation of this oxide layer may partly equalize the potential differences existing on the surface of the metal by insulating the grains from the electrolyte and thereby retarding the rate at which the corrosion proceeds.



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