325
6/24/64

MASTER

ORNL-3600
UC-25 - Metals, Ceramics, and Materials
TID-4500 (30th ed.)

EFFECTS OF HYDROGEN ON THE
HIGH-TEMPERATURE FLOW AND FRACTURE
CHARACTERISTICS OF METALS

H. E. McCoy, Jr.

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

EFFECTS OF HYDROGEN ON THE HIGH-TEMPERATURE FLOW
AND FRACTURE CHARACTERISTICS OF METALS

H. E. McCoy, Jr.

Facsimile Price \$ 18.00
Microfilm Price \$ 8.87

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

JUNE 1964

Submitted as a thesis to the Graduate Council of The University of
Tennessee in partial fulfillment of the requirements for the degree
of Doctor of Philosophy

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of Dr. E. E. Stansbury of the University of Tennessee and D. A. Douglas and J. R. Weir of the Oak Ridge National Laboratory who made numerous helpful suggestions during the course of this research and who also reviewed the manuscript for this document.

It would have been impossible to obtain all the test information reported in this document without the assistance of several technicians in the Mechanical Properties Group - K. W. Boling, E. Bolling, V. G. Lane, B. McNabb, C. W. Walker, and W. C. Williams. Metallographic studies were carried out with the assistance of Metallography Group technicians M. D. Allen, E. D. Bolling, and H. R. Tinch. The electron transmission microscopy was performed by J. O. Stiegler. O. B. Cavin and R. M. Steele conducted the x-ray studies described in this report. The assistance of the Oak Ridge National Laboratory Analytical Chemistry Division in determining the analysis of test material before and after testing was also quite essential.

The services of the Oak Ridge National Laboratory Graphic Arts Section and the Metals and Ceramics Division Reports Office were instrumental in preparing this document for publication. The specific assistance of Miss Susan Thompson in typing and preparing this report is gratefully acknowledged.

Finally, the author thanks the Oak Ridge National Laboratory for allowing him to participate in its education assistance program.

ABSTRACT

This report describes the results of a study directed toward an evaluation of the high-temperature mechanical behavior of several metals in hydrogen. Comparative creep-rupture testing in argon and hydrogen environments was the primary method used to evaluate the mechanical behavior. The materials studied included two heats of Inconel, Nickel 200, Nickel 270, an electron-beam zone-refined melt of nickel, high-purity copper, Armco iron, electrolytic iron, and type 304 stainless steel. All of the nickel-base materials and the copper exhibited inferior creep resistance in hydrogen, and the iron-base materials were not influenced by environment. Hydrogen had a large effect on pure nickel and copper with the magnitude decreasing with decreasing purity. This environmental effect was characterized, in general, by the following observations:

1. At the same stress and temperature, the minimum creep rate is greater in a hydrogen environment than in argon.
2. The rupture life is less in hydrogen than in argon at an equivalent stress and temperature.
3. The rupture ductility is not influenced.

Several additional experiments were run in an effort to determine the responsible mechanism. These experiments included measurement of permeation of hydrogen through Inconel, measurement of the surface energy of nickel in argon and in hydrogen, comparison of sintering rates of nickel powder in argon, hydrogen, and vacuum, comparison of

void formation in diffusion couples of iron and nickel annealed in argon and hydrogen environments, comparison of diffusion of carbon in nickel in hydrogen and in argon environments, measurement of the rate of self-diffusion of cobalt-60 in nickel in argon and hydrogen, and transmission electron microscopy on thin nickel creep specimens. The mechanism thought to be most consistent with the experimental observations was based on the interaction of hydrogen with dislocations. Although several details of the mechanism are lacking, this mechanism qualitatively accounts for most of the experimental observations.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. REVIEW OF LITERATURE	4
Creep and Fracture of Metals at Elevated Temperatures .	4
Hydrogen-Metal Interactions	13
The Effects of Metal-Hydrogen Interactions on the Mechanical Properties of Metals	23
III. EXPERIMENTAL DETAILS	33
Creep-Rupture Tests	33
Test Materials	35
Permeability Experiments	38
Surface Energy Measurements and Thin Foil Creep Experiments	38
Sintering Studies	42
Diffusion Experiments	42
Metallographic Techniques	49
IV. EXPERIMENTAL RESULTS	52
Stress Rupture	54
Stress-Rupture Properties of Inconel Sheet - Heat NX892	54
Stress-Rupture Properties of Inconel Rod - Heat R-892	72
Stress-Rupture Properties of Nickel 200 - Heat R-1031	95

CHAPTER

PAGE

Creep Properties of Electron-Beam Zone-Refined	
Nickel	123
Stress-Rupture Properties of Nickel 270	132
Stress-Rupture Properties of High-Purity Copper . . .	143
Stress-Rupture Properties of Armco Iron -	
Heat R-121	153
Stress-Rupture Properties of Electrolytic Iron . . .	165
Stress-Rupture Properties of Type 304 Stainless	
Steel	174
Creep Tests Involving Alternating Argon and Hydrogen	
Environments	174
Results of X-Ray Experiments	188
Permeability Experiments	191
Surface Energy Measurements in Argon and Hydrogen	
Environments	193
Sintering of Nickel Powders in Different Environments .	195
Comparison of the Size and Geometry of Voids Formed	
During the Interdiffusion of Iron and Nickel in	
Argon and Hydrogen	207
Influence of Argon and Hydrogen Environments on the	
Rate of Diffusion of Cobalt-60 in Nickel	212
Creep Studies on Thin Nickel Strips	217
A Comparison of the Rates of Diffusion of Carbon in	
Nickel in Argon and in Hydrogen Environments	228

CHAPTER	PAGE
V. DISCUSSION OF EXPERIMENTAL RESULTS	230
VI. SUMMARY AND CONCLUSIONS	246
REFERENCES	251
APPENDIX	257

LIST OF TABLES

TABLE	PAGE
I. Diffusion Constants of Hydrogen in Solid Metals . . .	22
II. Test Materials	36
III. Summary of Stress-Rupture Data on Inconel Sheet . . .	55
IV. Summary of Tensile Tests on Inconel Sheet	56
V. Crack Measurements on Inconel Sheet	73
VI. Summary of Creep Data on Inconel Rod	74
VII. Summary of Tensile Tests on Inconel Rod	76
VIII. Creep-Rupture Data Showing the Effect of Heat Treatment on the Creep of Inconel (R-892) at 3500 Psi and 815°C	80
IX. Summary of Tensile Tests on Nickel 200 at 815°C	96
X. Summary of Creep Data on Nickel 200 Rod	97
XI. Effect of Pretest Annealing Temperature on the Creep Properties of Nickel 200 at 815°C	105
XII. Effect of Pretreatment on the Creep Properties of Nickel 200 at 704°C and 3500 Psi	108
XIII. Summary of Tests Run on Electron-Beam Zone-Refined Nickel	124
XIV. Summary of Creep Data on Nickel 270 Rod	134
XV. Creep-Rupture Properties of High-Purity Copper at 800°C	144
XVI. Summary of Chemical Data on High-Purity Copper in Weight Per Cent	148

TABLE	PAGE
XVII. Summary of Tensile Tests on Armco Iron at 815°C	154
XVIII. Creep-Rupture Properties of Armco Iron	155
XIX. Summary of Chemistry Results for Armco Iron (R-121) . .	160
XX. Hardness Data on Armco Iron (R-121)	161
XXI. Creep Properties of Electrolytic Iron	168
XXII. Summary of Creep Data on Type 304 Stainless Steel . .	176
XXIII. Comparison of the Creep Rates of Nickel (Electron-Beam Zone-Refined) Single Crystal in Argon and Hydrogen Environments, Test 1992	178
XXIV. Comparison of the Creep Rates of Nickel (Electron-Beam Zone-Refined) Single Crystal in Argon and Hydrogen Environments, Test 1688	179
XXV. Comparison of the Creep Rates of Nickel (Electron-Beam Zone-Refined) in Hydrogen and Argon Environments, Test 2209	180
XXVI. Comparison of the Creep Rates of Nickel (R-1031) in Argon and Hydrogen Environments, Test 1979	184
XXVII. Comparison of the Creep Rates of Nickel (R-1031) in Argon and Hydrogen Environments, Test 1934, Annealed 1 Hr at 815°C Prior to Testing	185
XXVIII. Comparison of the Creep Rates of Nickel 200 (R-1031) in Hydrogen and Argon Environments, Test 1980	186
XXIX. Comparison of the Creep Rates of Nickel 200 (R-1031) in Hydrogen and Argon Environments, Test 2247	187

TABLE

PAGE

XXX.	Comparison of the Creep Rates of Copper (99.999 Per Cent) in Hydrogen and Argon Environments, Test 2757	189
XXXI.	Comparison of the Creep Rates of Iron (Electrolytic) in Hydrogen and Argon Environments	190
XXXII.	Sintering of Nickel Powder at 927°C, Test F	197
XXXIII.	Sintering of Nickel Powder in Hydrogen and Vacuum Environments, Test E	199
XXXIV.	Sintering of Nickel Powder in Different Atmospheres at 927°C	201
XXXV.	Density of Nickel Powder After Sintering 100 Hr in Argon or Hydrogen Environments at 927°C	206
XXXVI.	Test Conditions for Iron-Nickel Diffusion Couples	208
XXXVII.	Comparison of Results with Those of Other Investigators	216
XXXVIII.	Creep Tests Run Using Nickel Strip	221

LIST OF FIGURES

FIGURE	PAGE
1. Typical Creep Curves for Metals Under Various Conditions .	7
2. Classification of the Elements with Respect to Their Reactions with Hydrogen	14
3. Solubility of Hydrogen in Several Metals	20
4. Chamber for Environmental Stress-Rupture Tests at Elevated Temperatures	34
5. Specimens Used for Mechanical Property Tests	37
6. Apparatus for Studying Gas Permeability	39
7. Modified Microbalance for Surface Energy and Microcreep Experiments	41
8. Geometry of Diffusion Specimen	43
9. Compression Fixture for Diffusion Couples	46
10. Counting Fixture for Diffusion Specimens	50
11. Creep Curves of Inconel (NX892) at 815°C in Argon and Hydrogen Environments	57
12. Stress-Rupture Properties of Inconel at 815°C	58
13. Creep Rate of Inconel Sheet (NX892) in Argon and Hydrogen Environments	59
14. Rupture Ductility of Inconel Sheet (NX892) Specimens Tested in Argon and Hydrogen Environments	60
15. Correlation of Strain Rate and Rupture Life for Inconel Sheet (NX892) Tested in Argon and Hydrogen Environments .	61

FIGURE	PAGE
16. Photomicrograph of Inconel (NX892) Tested in Tension at 815°C at a Strain Rate of 2.5 Per Cent Per Hour. Environment Was Argon. Located 0.25 in. from Fracture .	64
17. Photomicrograph of Inconel (NX892) Tested at 10,000 Pounds Per Square Inch in Argon at 815°C. Test 972. Located 0.25 in. from Fracture	65
18. Photomicrograph of Inconel (NX892) Tested at 6000 Pounds Per Square Inch in Argon at 815°C. Test 1212. Located 0.25 in. from Fracture	66
19. Photomicrograph of Inconel (NX892) Tested at 5000 Pounds Per Square Inch in Argon at 815°C. Test 1143. Located 0.25 in. from Fracture	67
20. Photomicrograph of Inconel (NX892) Tested at 5000 Pounds Per Square Inch in Hydrogen at 815°C. Test 1215. Located 0.25 in. from Fracture	68
21. Photomicrograph of Inconel (NX892) Tested at 3500 Pounds Per Square Inch in Argon at 815°C. Test 906. Located 0.25 in. from Fracture	69
22. Photomicrograph of Inconel (NX892) Tested at 3500 Pounds Per Square Inch in Argon at 815°C. Test 906. Located 1 in. from Fracture	70
23. Photomicrograph of Inconel (NX892) Tested at 3500 Pounds Per Square Inch in Hydrogen at 815°C. Test 1141. Located 0.25 in. from Fracture	71

FIGURE	PAGE
24. Creep Properties of Inconel (R-892) at 704°C	77
25. Creep Properties of Inconel (R-892) at 815°C	78
26. Creep-Rupture Properties of Inconel (R-892) Tested at 3500 Pounds Per Square Inch and 815°C	81
27. Carbon Distribution in Tested Inconel Specimens	83
28. Photomicrograph of Inconel (R-892) in the As-Received Condition	85
29. Photomicrograph of Inconel (R-892) Tested at 2500 Pounds Per Square Inch in Argon at 815°C. Test 1249. Located 0.75 in. from Fracture	86
30. Inconel (R-892) Tested at 2500 Pounds Per Square Inch in Hydrogen at 815°C. Test 1186. Located 0.75 in. from Fracture	87
31. Inconel (R-892) Tested at 2000 Pounds Per Square Inch in Hydrogen at 927°C. Test 1344. Located 0.75 in. from Fracture	88
32. Inconel (R-892) Tested at 3500 Pounds Per Square Inch in Argon at 815°C. Material Tested in the As-Received Condition. Test 1491. Located 0.75 in. from Fracture .	90
33. Inconel (R-892) Tested at 3500 Pounds Per Square Inch in Argon at 815°C. Material Annealed 1 hr at 1038°C Prior to Testing. Test 1554. Located 0.75 in. from Fracture	91

FIGURE	PAGE
34. Inconel (R-892) Tested at 3500 Pounds Per Square Inch in Argon at 815°C. Material Carburized in CO and Annealed 1 hr at 1038°C in Argon Prior to Testing. Test 1441. Located 0.75 in. from Fracture	92
35. Inconel (R-892) Tested at 3500 Pounds Per Square Inch in Hydrogen at 815°C. Material Carburized in CO and Annealed 1 hr at 1038°C in Argon Prior to Testing. Test 1439. Located 0.75 in. from Fracture	93
36. Inconel (R-892) Tested at 3500 Pounds Per Square Inch in Argon at 815°C. Material Annealed 1 hr at 1204°C in Argon Prior to Testing. Test 1552. Located 0.75 in. from Fracture	94
37. Creep-Rupture Properties of Nickel 200 in Argon and Hydrogen Environments	99
38. Creep of Nickel 200 in Argon and Hydrogen Environments at 704°C	101
39. Ductility of Nickel 200 Tested in Argon and Hydrogen Environments	102
40. Creep Properties of Nickel 200 (R-1031)	103
41. Influence of Annealing Temperature on the Creep of Nickel 200 in Argon and Hydrogen Environments	106
42. Influence of Prestraining on the Creep Properties of Nickel 200 at 704°C and 3500 Pounds Per Square Inch	109

FIGURE	PAGE
43. Photomicrograph of Nickel 200 (R-1031) Annealed 1 hr at 815°C in Vacuum	110
44. Photomicrograph of Nickel 200 (R-1031) Annealed 1 hr at 1038°C in Vacuum	111
45. Nickel 200 (R-1031) Tested at 11,000 Pounds Per Square Inch in Argon at 704°C. Test 1633. Upper Photograph Taken Approximately 0.75 in. from Fracture. Lower Photograph Taken at Fracture	112
46. Nickel 200 (R-1031) Tested at 5000 Pounds Per Square Inch in Argon at 704°C. Test 1409. Upper Photograph Taken Approximately 0.75 in. from Fracture. Lower Photograph Taken at Fracture	113
47. Nickel 200 (R-1031) Tested at 3500 Pounds Per Square Inch in Argon at 704°C. Test 1476. Photograph Taken at Fracture	114
48. Nickel 200 (R-1031) Tested at 3500 Pounds Per Square Inch in Argon at 704°C. Test 1476. Upper Photograph Taken Near Center of Specimen 0.75 in. from Fracture. Lower Photograph Taken at the Edge of Specimen Approximately 0.75 in. from Fracture	115
49. Nickel 200 (R-1031) Tested at 3500 Pounds Per Square Inch in Hydrogen at 704°C. Test 1475. Upper Photograph Taken Near Center of Specimen 0.75 in. from Fracture. Lower Photograph Taken at the Edge of the Specimen Approximately 0.75 in. from Fracture	116

FIGURE	PAGE
50. Nickel 200 (R-1031) Tested at 3500 Pounds Per Square Inch in Argon at 704°C. Material Was Strained 5 Per Cent. Prior to Testing. Test 1983	119
51. Nickel 200 (R-1031) Tested at 3500 Pounds Per Square Inch in Hydrogen at 704°C. Material Was Strained 5 Per Cent Prior to Testing. Test 1981	120
52. Micrograph of Sectioned Nickel 200 (R-1031) Specimen Tested at 2000 Pounds Per Square Inch in Hydrogen at 815°C. Specimen Annealed 1 hr at 815°C in Vacuum Prior to Testing. Test 1349. Upper Micrograph. Photomicrograph of Specimen Taken Near the Specimen Edge About 0.75 in. from the Fracture. Lower Photomicrograph	121
53. Micrograph of Sectioned Nickel 200 (R-1031) Specimen Tested at 2000 Pounds Per Square Inch in Hydrogen at 815°C. Specimen Annealed 1 hr at 1038°C in Vacuum Prior to Testing. Test 1374. Upper Micrograph. Photomicrograph of Specimen Taken Near the Specimen Edge About 0.75 in. from the Fracture. Lower Photomicrograph	122
54. Creep of Electron-Beam Zone-Refined Nickel in Argon and Hydrogen at 2100 Pounds Per Square Inch and 815°C . . .	125
55. Nickel Specimen Tested at 2100 Pounds Per Square Inch in Hydrogen at 815°C. Test 1995. Upper Photograph - Fracture; Lower Photograph - Representative About 0.50 in. from Fracture	126

FIGURE	PAGE
56. Nickel Specimen Tested at 2100 Pounds Per Square Inch in Argon at 815°C. Test 1998	127
57. Nickel Specimen from Test 1688	129
58. Nickel Tested Over the Temperature Range of 815–927°C Under Creep Conditions in Alternating Argon and Hydrogen. Test 1688	130
59. Electron-Beam Zone-Refined Nickel in the As-Received Condition	131
60. Nickel Tested at 815°C Under Creep Conditions in Alternating Argon and Hydrogen Environments. Test 1992	133
61. Rupture Life of Nickel 270 at 800°C	135
62. Minimum Creep Rate of Nickel 270 at 800°C	137
63. Photomicrograph of Nickel 270 in the As-Received Condition	138
64. Photomicrograph of Nickel 270 After a 1-hr Anneal in Vacuum at 800°C	139
65. Nickel 270 Tested in a Hydrogen Environment at 800°C and 1000 Pounds Per Square Inch. Test 2440. Photograph Taken at the Fracture with the Specimen in the As-Polished Condition	140
66. Nickel 270 Tested in a Hydrogen Environment at 800°C and 1000 Pounds Per Square Inch. Test 2440. Photograph Taken 1 in. from Fracture	141

FIGURE	PAGE
67. Nickel 270 Tested in an Argon Environment at 800°C and 1000 Pounds Per Square Inch. Test 2612. Photograph Taken 1 in. from Fracture	142
68. Creep Properties of High-Purity Copper at 800°C	145
69. Minimum Creep Rate of High-Purity Copper at 800°C	146
70. Photomicrograph of High-Purity Copper Annealed 1 hr at 800°C in Vacuum	149
71. High-Purity Copper After Testing at 600 Pounds Per Square Inch and 800°C in Argon. Test 2296	150
72. High-Purity Copper After Testing at 300 Pounds Per Square Inch and 800°C in Hydrogen. Test 2471	151
73. High-Purity Copper After Testing at 500 Pounds Per Square Inch and 800°C in Argon. Annealed 162 hr at 800°C in Hydrogen Prior to Testing. Test 2205	152
74. Stress-Rupture Properties of Armco Iron Tested in Argon and Hydrogen at 815°C	156
75. Creep Properties of Armco Iron Tested in Argon and Hydrogen at 815°C	157
76. Ductility of Armco Iron Creep Specimens Tested at 815°C in Argon and Hydrogen	159
77. Photomicrograph of Armco Iron (R-121) in the As-Received Condition	162

FIGURE	PAGE
78. Armco Iron (R-121) Stressed at 500 Pounds Per Square Inch in Argon at 815°C. Ruptured After 368.1 hr with 8.75 Per Cent Strain. Photomicrographs Located 1 in. from Fracture	163
79. Armco Iron (R-121) Stressed at 500 Pounds Per Square Inch in Hydrogen at 815°C. Ruptured After 477.3 hr with 8.76 Per Cent Strain. Photomicrographs Located 1 in. from Fracture	164
80. Armco Iron (R-121) Stressed at 300 Pounds Per Square Inch in Argon at 815°C. Ruptured After 2285.5 hr with 8.76 Per Cent Strain. Photomicrograph Located 0.75 in. from Fracture	166
81. Armco Iron (R-121) Stressed at 300 Pounds Per Square Inch in Hydrogen at 815°C. Ruptured After 1956.1 hr with 13.0 Per Cent Strain. Photomicrograph Located 0.75 in. from Fracture	167
82. Rupture Life of Electrolytic Iron at 800 and 950°C	169
83. Minimum Creep Rate of Electrolytic Iron at 800 and 950°C .	170
84. Photomicrograph of Electrolytic Iron After Annealing 1 hr at 1000°C in Hydrogen	172
85. Photomicrograph of Electrolytic Iron After Testing at 800°C and 500 Pounds Per Square Inch in Argon. Test 2343. Photograph Taken 0.75 in. from Fracture	173

FIGURE

PAGE

86. Photomicrograph of Electrolytic Iron After Testing at 800°C and 500 Pounds Per Square Inch in Hydrogen. Test 2454. Photograph Taken 0.75 in. from Fracture . . .	175
87. Creep of Nickel Single Crystal in Argon and Hydrogen Environments at 815°C and 2183 Pounds Per Square Inch. Test 1992	182
88. Permeation of Hydrogen Through Inconel at 815°C	193
89. Sintering of Nickel Powder at 927°C	198
90. Sintering of Nickel Powder	200
91. Nickel Powder Annealed 24 hr at 1000°C in Hydrogen and Sintered 498 hr at 927°C in Vacuum. Test I	203
92. Nickel Powder Annealed 24 hr at 1000°C in Hydrogen and Sintered 495 hr at 927°C in Hydrogen. Test J	204
93. Nickel Powder Annealed 24 hr at 1000°C in Hydrogen and Sintered 487 hr at 927°C in Argon. Test K	205
94. Comparative Iron-Nickel Diffusion Couples at 927°C	209
95. Comparative Iron-Nickel Diffusion Couples at 1091°C	210
96. Comparative Iron-Nickel Diffusion Couples at 1204°C	211
97. Penetration Plot of the Diffusion of Cobalt-60 into Nickel After 446.2 hr at 1193°C	213
98. Penetration Plot of the Diffusion of Cobalt-60 into Nickel After 1171 hr at 1095°C	214
99. Creep of Nickel Strip in Argon and Hydrogen Environments at Elevated Temperatures	218

FIGURE	PAGE
100. Creep of Nickel Strip in Argon and Hydrogen Environments at 700°C	220
101. Transmission Electron Micrograph of Nickel Specimen from Test 2240	223
102. Transmission Electron Micrograph of Nickel Specimen from Test 2266	224
103. Transmission Electron Micrograph of Nickel Specimen from Test 2164	225
104. Transmission Electron Micrograph of Nickel Specimen from Test 2266	226
105. Photomicrographs of Nickel Strips Tested at Elevated Temperatures. (a) Test 2164. (b) Test 2163. (c) Test 2240. (d) Test 2266	227
106. Effect of Environment on the Diffusion of Carbon in Nickel During a 300-hr Anneal at 704°C	229

CHAPTER I

INTRODUCTION

It is becoming apparent rapidly that the mechanical properties of a metal are not uniquely dependent upon the temperature, but rather that numerous other variables such as purity, prior thermal and mechanical histories, and test environment must be considered. Studies of the effects of such variables are of value from two viewpoints. First, such information is of practical importance and has made possible the construction and successful operation of engineering structures under very severe service conditions. Secondly, studies of the dependence of deformation on such variables have led to a better knowledge of the fundamental processes which control the mechanical behavior of metals. For example, studies have shown that different microstructures produced by heat treatment of alloys result in marked changes in mechanical behavior. In many materials a finely dispersed precipitate is formed by heat treatment and the characteristics (spacing, coherency, stability, etc.) of this precipitate control the properties of the alloy.

The work to be discussed presently is concerned with the influence of hydrogen on the mechanical properties of metals at elevated temperatures. There are several practical reasons for considering this problem. One reason is that hydrogen has properties which make it very attractive as a coolant for a gas-cooled nuclear reactor. The lack of information concerning the mechanical behavior of structural materials

in hydrogen may soon become the limiting factor in the design and construction of a hydrogen-cooled reactor. The presence of hydrogen as an impurity in nuclear systems due to the dissociation of hydride moderators or from the dissociation of water has already been encountered. The use of hydrogen both as a fuel and as a heat transfer medium for space applications presents additional needs for the knowledge of the performance of metals in a hydrogen environment.

The major emphasis in the present study was placed upon nickel and nickel-base alloys. However, several other metals were studied briefly for the purpose of a broader evaluation of the types of materials that might be altered by hydrogen. These metals include copper (99.999 per cent), type 304 stainless steel, Armco iron, and electrolytic iron. Creep testing over the temperature range of 600 to 950°C was the principal method used to determine whether the mechanical behavior of a metal was different in hydrogen than in an argon environment. The test specimens were examined metallographically and chemically after testing. Several other types of experiments were conducted in an effort to pinpoint the mechanism responsible for the hydrogen effect. These experiments include measurement of permeation of hydrogen through Inconel, measurement of the surface energy of nickel in argon and in hydrogen, comparison of sintering rates of nickel powder in argon, hydrogen, and vacuum, comparison of void formation in diffusion couples of iron and nickel annealed in argon and hydrogen environments, comparison of the diffusion of carbon in nickel in hydrogen and in argon environments, measurement of the rate of self-diffusion of

cobalt-60 in nickel in argon and in hydrogen, and transmission electron microscopy on thin nickel creep specimens. Although some of these experiments may appear to be somewhat unrelated, they represent significant steps in arriving at the present state of knowledge of the mechanical behavior of metals in a hydrogen environment at elevated temperatures. The reasoning which preceded the performance of each experiment will be given as the results of the individual experiments are discussed.

CHAPTER II

REVIEW OF LITERATURE

I. CREEP AND FRACTURE OF METALS AT ELEVATED TEMPERATURES

The creep of metals has been reviewed quite thoroughly (1-3) and a recapitulation of the large volume of published information is not in order in the present document. However, an attempt will be made to generate a somewhat simplified, but qualitatively correct, picture of creep in metals.

If a continuously increasing stress is applied to a perfect crystal, the material is expected to deform elastically until the resolved shear stress on a plane exceeds the forces which hold the atoms together. At this point the crystal begins to deform plastically. Frenkel (4), using a very simple atomic model, proposed that the theoretical shear strength of a material should be approximately one-sixth its shear modulus. Mackenzie (5) has refined Frenkel's calculation and obtained a factor of one-thirtieth. However, the shear strengths actually observed for real crystals are at least one order of magnitude less than that predicted by Mackenzie's calculation. The pronounced discrepancy between the yield strength of a perfect crystal and a real crystal is ascribed to the presence and motion of imperfections that exist in real crystals. Although numerous types of imperfections have been defined, the most important in deformation processes are vacancies and dislocations. The motion of these defects makes it possible for two planes of atoms to be displaced with respect to one another by the

motion of a few atoms at a time rather than having to break the atomic bonds between the two planes.

Although the presence of dislocations was first predicted by Taylor (7), Orowan (8), and Polanyi (9) largely from inductive reasoning, recent improvements in the electron microscope have made it possible to observe these defects in thin foils of metals (6). These line defects are observed to move and to interact with one another essentially as predicted. The field emission microscope (10) has also made possible the direct observation of dislocations as well as vacancies in metals. Dislocations are not thermodynamically stable but nevertheless are found in all metals in large concentrations. In carefully grown metal crystals, the dislocation density is found to be of the order of 10^2 to 10^6 dislocations/cm². In highly deformed metals, the density may be as high as 10^{12} dislocations/cm². On the other hand a certain concentration of vacancies is thermodynamically stable in a metal, depending primarily upon the temperature. The increase in energy due to the vacancies is compensated by an increase in entropy resulting from the increase in randomness of the structure. Since the entropy increases with temperature, the concentration of vacancies likewise increases with temperature. For example, the fraction of vacant lattice sites in copper is 10^{-17} at 300°K, $10^{-6.2}$ at 800°K, and $10^{-3.9}$ at 1300°K.

Just as the presence of these defects has offered a reasonable explanation for the less-than-theoretical yield strength of metals in a test where the stress is being continually increased, their presence

also accounts for the deformation of metals under quite low constant stresses. The time-dependent plastic deformation of a metal under a constant stress is referred to as creep. Creep deformation is normally observed to follow one of the forms shown schematically in Figure 1. This behavior can be rationalized in the following way. When the load is first applied, an instantaneous elastic strain occurs. In addition the stress usually will be high enough to cause some of the dislocations to move, resulting in plastic deformation until some force stops their motion. This force may come from several obstacles which serve as barriers to dislocation motion. These include precipitates or impurity clusters, grain boundaries (in a polycrystalline material), and dislocation intersections which produce sessile or immobile dislocation segments. All of these processes decrease the number of mobile dislocations and the deformation rate decreases with time over a period which is termed the primary stage of creep. What happens next depends primarily upon the temperature of the material. There are two important processes which allow a dislocation to escape a barrier. One is conservative motion in its own slip plane. The dislocation loops around the obstacle and rejoins on the opposite side. This produces a free dislocation and a dislocation loop around the obstacle which may be able to expand. The other process involves the climb of the dislocation over the obstacle. This involves diffusion of atoms and hence generally becomes important at temperatures above 0.4, the absolute melting temperature of the metal. If the temperature is low and the stress is not sufficient to allow the dislocations to loop around their barriers,

UNCLASSIFIED
ORNL-DWG 63-6436

Figure 1. Typical creep curves for metals under various conditions.

the number of mobile dislocations will continue to decrease until the deformation rate becomes nil. This behavior is represented by curve A (Figure 1, page 7). If the stress is sufficiently high to allow some of the dislocations to loop around their barriers or if the temperature is high enough for climb to occur, a steady state will be established between the number of new dislocations being generated or free and the number being pinned by some barrier or annihilated. This leads to a linear deformation rate such as that shown in curve B (Figure 1, page 7). This steady-state condition will be upset eventually, and the deformation rate will increase with fracture resulting. If the temperature and stress are quite high, the dislocation barriers are not as effective and a steady-state condition between the rates of generation and pinning or annihilation of dislocations is never established. The deformation rate continues to increase with time, as shown by curve C, until fracture occurs.

The subject of fracture in metals, even though it has received much attention (11), is not understood as well as creep. Several metallographic observations have been made which give some insight into the processes which must lead to fracture. Metals which fail without much plastic deformation (brittle) normally are found to contain only a few cracks near the fracture. They are normally transgranular unless the cause of the brittle behavior is related to the grain boundary layer in which case the cracks are largely intergranular. Materials which undergo considerable plastic deformation prior to fracture (ductile) exhibit three basic types of structures. One type of behavior

is characterized by transgranular cracks and is formed in materials tested at low temperatures or moderate temperatures and high strain rates. A second type of microstructure consists of very large intergranular cracks. This occurs in materials tested above half the absolute melting temperature and at high strain rates. A third type of structure consists of intergranular cracks which are largely made up of small voids joined together. High temperatures and low strain rates favor this structure.

A large number of mechanisms have been proposed for the nucleation of cracks in metals. Several of these which involve dislocation interactions are reviewed by McLean (12). Inclusions have also been found to lead to stress concentrations sufficient to form crack nuclei. Zener (13) has proposed that shear stresses acting along grain boundaries which meet at a triple point can nucleate cracks. Gifkins (14) and Chen and Machlin (15) independently proposed similar mechanisms for crack nucleation at grain boundaries at elevated temperatures. Slip steps or other discontinuities in the grain boundary between two adjacent grains were proposed to be able to nucleate a crack if a sufficiently large shear stress is applied along the grain boundary. The sources of crack nuclei are indeed so numerous that it would seem that the growth of these nuclei into stable cracks and the propagation of these cracks must be the important processes rather than crack nucleation per se.

In a brittle material, the only energy which must be supplied to propagate a crack is the energy required to form new surfaces. This

concept has been developed by Griffith and is represented mathematically by

$$\sigma_c = \left(\frac{2E\gamma}{\pi C} \right)^{1/2} . \quad (1)$$

The critical stress for crack propagation is σ_c , E is Young's modulus, C is the crack length, and γ is the surface energy. If the material exhibits some plasticity, the Griffith criterion no longer applies. In this case a strain energy term due to plastic flow at the tip of the propagating crack must be added to the energy required to form new surfaces.

At elevated temperatures, another mechanism of crack growth becomes operative, the condensation of vacancies. Machlin (16) has shown that the degree of vacancy supersaturation could never reach the necessary levels for void nucleation during a creep test. However, he proposed that it was probable that pre-existing voids would grow under creep-rupture conditions by vacancy condensation. Machlin made several predictions based on this process and presented experimental data which verified these predictions. Balluffi and Seigle (17) made a study of the thermodynamic conditions under which voids could grow by vacancy condensation during both creep and Kirkendall diffusion. If a void exists in a metal, the surface energy of this void provides a driving force for its collapse. However, an applied stress can overcome this collapsing tendency and cause the void to grow. The important variables in this process are related by:

$$\sigma^* = \frac{2\gamma}{r \cos^2 \theta} \quad (2)$$

where σ^* is the applied stress necessary for void growth, γ the surface energy, r the radius of the void, and θ the angle between the applied stress and the plane containing the void. This equation predicts that the stress required to cause a void to grow is a minimum when the void lies in a plane normal to the applied stress. This is in agreement with experimental observations (18). The main difference in the thinking of Machlin (16) and Balluffi and Seigle (17) is that Machlin is concerned only with the growth of voids due to vacancy supersaturation and Balluffi and Seigle are concerned with growth by the diffusion of vacancies due to the effect of stress and orientation on their chemical potential. The former reasoning would predict that voids would grow in compression tests, whereas the latter would predict no void growth under compressive loading. This critical experiment has not been reported to date. Greenwood et al. (18) observed that voids were formed during the high-temperature creep of copper, alpha-brass, and magnesium. These voids were present quite early in the creep tests. McLean (19) examined ruptured specimens of several commercial nickel-base alloys and found that they contained intergranular cracks of two types. The specimens tested at low stresses contained intergranular cracks made up of isolated voids. The specimens tested at high stresses contained large wedge-shaped cracks which appeared to form as a result of large stress concentrations. McLean rationalized that the diffusional processes which lead to void development and growth were operative at all stress levels, but that a critical stress was necessary to activate the processes which lead to the formation of the

wedge-shaped cracks. At high stresses the latter process predominates and at low stresses the former predominates. Shinoda et al. (20) have made similar observations on AISI type 304, type 304L, and a 19.58 per cent Cr-20.86 per cent Ni stainless steel tested in creep at 600°C.

The formation of voids in specimens under creep conditions has generally been associated with low rupture ductilities (18). Hence considerable effort has been expended in studying void formation in metals. Several variables are shown to be of importance. Resnick and Seigle (21) have shown that impurities (probably ZnO) are important in the formation of voids in alpha-brass during creep and vacuum dezincification. Pure brass was found to exhibit less tendency for void formation than impure brass which contained visible inclusions. At least one experimenter (22) has attributed the tendency of voids to be formed in some materials, under certain conditions and not in others, to the variation in the ability for grain boundary migration to occur. The reasoning is that, if the grain boundaries are pinned by impurities or pre-existing voids, they will be unable to move and intergranular voids will form and continue to grow. If the boundary is able to move, then grain boundary voids will not have time to form. Although intergranular voids have been observed in high-temperature creep specimens by several experimenters and their nucleation and growth can be rationalized, their exact role in high-temperature creep has not been defined.

II. HYDROGEN-METAL INTERACTIONS

Cotterill (23) and Smith (24) have classified the metals with respect to their interaction with hydrogen, as shown in Figure 2. The alkali and alkaline-earth metals react with hydrogen to form saltlike hydrides. These compounds, which are ionic and generally crystalline, are analogous to the corresponding halides. The metals of groups IVB, VB, and VIB form covalent hydrides which are gaseous at room temperature. These compounds are analogous to the hydrocarbons. The remaining metals are either inert or absorb hydrogen. Further divisions are made with respect to whether the absorption reactions occur endothermally or exothermally. It is this third group of metals which is of importance in connection with this study, and the characteristics of the reactions of these materials with hydrogen will be considered in some detail.

The endothermic absorbers form relatively simple solid-solution alloys with hydrogen with the solubility of hydrogen increasing with increasing temperature. Smith (24) questioned whether these metals actually formed solid solutions with hydrogen. He proposed his classical "rift" model in which the hydrogen is present only in defects in the metal. These "rifts" or defective areas can be opened up to absorb hydrogen by heating, by cold working, or by the absorption process itself. Several experimenters have challenged Smith's (24) "rift" model. For example, Ransley (25) has written: "Indeed, it is not unfair to say that in a good many instances the author (i.e.,

UNCLASSIFIED
ORNL DWG. 64-3203 **KEY**

IONIC HYDRIDE FORMING ELEMENTS

COVALENT HYDRIDE FORMING ELEMENTS

EXOTHERMIC OCCLUDERS-FORMING "PSEUDO-METALLIC" HYDRIDES

ENDOTHERMIC OCCLUDERS-FORMING ONLY SOLID SOLUTIONS AND/OR
HYDRIDES WHICH ARE VERY UNSTABLE

RE

RARE EARTH ELEMENTS

Figure 2. Classification of the elements with respect to their reactions with hydrogen (23).

Smith) has strained the facts very severely in an attempt to make them conform to this theory, when a simple explanation based on lattice solution and diffusion would appear to be perfectly adequate." The experimental observation that the solubility of hydrogen in several metals is proportional to the square root and not to the first power of the hydrogen pressure is evidence that a metal-hydrogen solid solution is being formed. The pressure dependence of the solubility of gases in liquids, when no chemical reaction occurs, is governed by Henry's law:

$$s = k \cdot p \quad (3)$$

where s is the solubility, p the pressure, and k a constant dependent on the temperature. If a diatomic gas (for example, hydrogen) must dissociate before it can dissolve in a metal, the reaction may be written as:

(4)

where $\underline{H}^+$ indicates hydrogen dissolved in the metal. The overall reaction is represented by reaction (4c) which has an equilibrium constant, k_p , given by

$$k_p = \frac{[\underline{H}^+]^2}{P_{H_2}} \quad (5)$$

where P_{H_2} denotes the hydrogen pressure. Equation (5) can be rewritten

to show that the concentration of hydrogen in solution is proportional to $P_{H_2}^{1/2}$. Hence the square root pressure dependence of the solubility of hydrogen indicates that the hydrogen is indeed going into solution in the metal and not simply filling "rifts" as proposed by Smith.

The exothermic absorbers of the third group are characterized by the formation of what Dushman (26) refers to as "pseudo-hydrides." The quantity of hydrogen absorbed by these materials is said to decrease with increasing temperature. However, this is somewhat confusing since a clear distinction has not been made between the amount of hydrogen soluble and the total amount that can be absorbed. Generally speaking, it has been found that the solid solubility of hydrogen increases in these metals with increasing temperature, but the total amount of hydrogen absorbed decreases due to the exothermic nature of hydride formation (1).

Barrer (27) has questioned the distinction made by others as to materials being endothermic and exothermic absorbers. The distinction is normally based on the energy associated with reaction (4c) which is normally termed the molar heat of absorption, ΔH_m . However, equilibrium does not occur directly between molecular hydrogen and dissolved hydrogen but rather between dissociated hydrogen and dissolved hydrogen. Hence, Barrer (27) suggested that the heat of absorption be referred to a constant pressure of atomic hydrogen rather than to the total gas pressure. This heat of absorption he referred to as the atomic heat of sorption, ΔH_a , which was expressed as:

$$\Delta H_a = \frac{\Delta H_m - \Delta H_d}{2} . \quad (6)$$

The heat of dissociation of molecular hydrogen is ΔH_d , which at 298°K is equal to $105,000 \pm 3,500$ calories/mole (28). Because of the relatively large magnitude of ΔH_d as compared with ΔH_m , the absorption of atomic hydrogen is strongly exothermic for all metals of the third class.

Those who feel that metals of the third group do form true solid solutions with hydrogen generally agree that the hydrogen atoms are present in interstitial positions in the metal lattice. Although the hydrogen atom is relatively small with a corrected radius of 0.48 Angstrom (29), it still results in some distortion of the metal lattice. For example, the interstitial holes in the body-centered cubic form of iron have a radius of 0.36 Angstrom and those of face-centered cubic iron are 0.52 Angstrom (30). The importance of crystal size on the solubility of hydrogen is illustrated by the fact that the solubility is greater in gamma- than in alpha-iron. However, electronic effects are also important as illustrated by the extremely small solubility of helium in these metals.

Another important phenomenon associated with the presence of hydrogen in metals is that large pressures can be generated in voids, blisters, and other cavities. This can occur when the metal is saturated with hydrogen at an elevated temperature and rapidly cooled to a lower temperature. The decrease in the solubility of hydrogen with decreasing temperature results in the liberation of hydrogen

which collects in the voids. Since hydrogen is only slightly dissociated at reasonable temperatures (0.08 per cent at 2000°K) (31), quite large pressures can be developed by this process. Luckemeyer-Hasse and Schenck (32) first pointed out the importance of this process in iron and computed attainable pressures on the basis of the hydrogen solubility being a linear function of the temperature. Phragmén has refined this computation to obtain

$$T = \frac{3000 - 0.062 p}{\log p - 2 \log x + 3.6} \quad (7)$$

where p is the pressure in atmosphere, x the hydrogen content in cubic centimeters per 1000 grams of iron, and T the absolute temperature in °K. This formula, for example, indicates that, when the specimen contains 5 cm³ hydrogen per 100 grams iron [the solubility in iron at approximately 950°C (32)], the pressure of hydrogen in cavities is 17 atmospheres at 600°C, 800 atmospheres at 300°C, and 17,500 atmospheres at 20°C. There are several obvious criticisms which should be made of the methods used to obtain these numbers. The first is that the equilibrium conditions associated with the bulk gas phase have been used to make the computation. The conditions existing inside a void could require a completely different equilibrium condition. Another objection is that no allowance has been made for the escape of hydrogen from the specimen during cooling which obviously depends on the geometry of the pieces and would be difficult to incorporate. More important than the pressures quoted above are the observations of Krupkowski and Smialowski (34) on the deformation of iron rods during electrolytic charging. Based upon the dimensional changes of the iron

and metallographic observations concerning the size and depth of voids, these experimenters estimated the pressure in the voids to be of the order of 10^5 atmospheres.

Several characteristics of the reactions of hydrogen with metals have been discussed in fairly general terms, but now it is desired to deal specifically with the metals used in the present study. The solubility of hydrogen in these materials (iron, nickel, copper and chromium, as an alloy addition) is presented in Figure 3. All of these metals fall into the third class as endothermic absorbers. However, nickel has been shown fairly conclusively to form a hydride compound. X-ray diffraction studies by Janko (35) have shown that nickel layers freshly charged with cathodically evolved hydrogen reveal a characteristic pattern in which distinct lines of a new crystalline phase are visible. The pattern of the new phase corresponds to a face-centered cubic crystal lattice having a lattice parameter of 3.71 Angstroms which is about 6 per cent larger than nickel. The intensity of the nickel hydride pattern gradually decreased after the interruption of the polarizing currents. Nickel hydride was not observable 5 hours after the current was interrupted. Wurtz (36) observed that a cuprous hydride compound could be formed from an aqueous solution. This compound, as well as the nickel hydride, appears to be very metastable and would not be of importance in high-temperature studies. There are no authenticated reports of hydride formation with either chromium or iron.

Because of the small size of the hydrogen atom, it diffuses relatively fast through most metals. The available data on the

Figure 3. Solubility of hydrogen in several metals.

diffusion of hydrogen in iron, nickel, and copper are given in Table I.

One other important type of hydrogen-metal interaction which has not been discussed is that involving the removal of interstitial impurities from metals. The reaction of hydrogen with dissolved carbon, sulfur, oxygen, and nitrogen is possible in the metals considered in this study. If one considers the rate of the reaction to be controlled by the rate of diffusion of the interstitial elements through the bulk metal, then the rate of removal of these elements should be very rapid in hydrogen. However, as pointed out by Fast (37), several other steps are involved in the solution (or evolution) of a gas in a metal. Fast describes the process of permeation through a metal as depending on the following steps:

1. The dissociation of the gas molecules in the layer adsorbed on the metal surface.
2. The transfer of the gas from the adsorbed layer to true solution within the metal.
3. The diffusion of gas through the metal.
4. The transfer of gas from solution to the adsorbed layer on the exit side of the metal.
5. The recombination of the gas atoms to the molecular form on the exit side of the metal.

Hence, the rate of removal of an impurity from a metal as a gaseous product not only depends on the diffusion rate of the impurity but also on certain surface reactions. This is strongly supported by the

TABLE I

DIFFUSION CONSTANTS OF HYDROGEN IN SOLID METALS^a

$$(D = D_0 e^{-E_D/RT})$$

Metal	D_0 (cm ² /sec)	E_D (cal/g atom)	Remarks
Cu	6.8×10^{-2}	11,300	250-600°C
	1.1×10^{-2}	9,200	---
α -Fe	1.65×10^{-2}	9,200	Electrolytic
Ni	4.47×10^{-3}	8,600	Degassing
	7.6×10^{-2}	9,880	Degassing
	9.5×10^{-3}	10,300	Degassing
	2.04×10^{-3}	8,700	Degassing

^aColin J. Smithells, Metals Reference Book,
3rd ed., p 580, Butterworths, London, 1962.

experimental observation that the presence of water vapor increases the kinetics of all of these reactions. For example, Jenkins (38) showed that pure hydrogen is only a weak decarburant for iron at temperatures up to about 1000°C and that a hydrogen-water vapor mixture is strongly decarburizing under similar conditions.

III. THE EFFECTS OF METAL-HYDROGEN INTERACTIONS ON THE MECHANICAL PROPERTIES OF METALS

The creep and fracture of metals and the various possible hydrogen-metal chemical interactions have been discussed. An attempt will be made to show how these hydrogen-metal interactions influence the mechanical properties of metals. The first two groups of metals which form saltlike compounds and gaseous compounds, respectively, are not of concern in the present study and the consequences of such chemical reactions on the mechanical properties of these materials will not be discussed. All of the attention in this section will be directed toward the third class of metals which absorb hydrogen. The major interest in the influence of hydrogen on the mechanical properties of metals has been with respect to embrittlement and at least one comprehensive review (23) has been made of the subject. Although the hydrogen effects to be reported in this study do not result in embrittlement, the subject of hydrogen embrittlement will be reviewed briefly since some of the features of this interaction are of general applicability.

The exothermic absorbers of the third class of materials which form pseudo-hydrides are generally found to be brittle when they contain

the hydride phase. Such embrittlement has been reported for titanium (39), titanium alloys (40), zirconium (44), uranium (42), columbium (43), and vanadium (44, 45). The hydrides formed in these materials are brittle and serve as sources of cracks as well as barriers to dislocation motion. It is indeed not surprising that these metals are brittle at relatively low temperatures when they contain a hydride precipitate. From a practical standpoint, these hydrides become unstable in vacuum at moderate temperatures, and it is possible to remove the hydrogen and thus eliminate this type of embrittlement.

Another type of hydrogen embrittlement is referred to as "slow strain-rate embrittlement." This type of embrittlement is well documented for iron but also occurs in nickel. Cotterill (23) in reviewing the subject of hydrogen embrittlement in iron summarized the physical effects as follows:

1. Hydrogen has no significant effect on the elastic properties.
2. The hardness remains unaffected by hydrogen in the range 0 to 10 cm³ hydrogen per 100 grams of iron (46) although the ultimate tensile strength is decreased (47).
3. The fracture stress is lowered in proportion to the hydrogen concentration (47, 48).
4. Hydrogen can produce a small yield point in pure iron at low temperatures (49). At normal temperatures the presence of hydrogen can prevent the occurrence of the yield phenomena which are usually found in mild steel (50).

5. Both the ductility parameters (elongation and reduction of area) are reduced in proportion to the hydrogen content up to about 5 cm³ per 100 grams of iron. Above this figure the ductility has a constant, low value (46, 47).
6. Hydrogen embrittlement is reduced as the rate of strain is increased (40), the limiting case being that of the impact test on which hydrogen has virtually no effect (47, 51).
7. The embrittlement effect occurs in the temperature range from -100 to +100°C, the maximum effect being at, or just below, room temperature.
8. There are no reported instances of hydrogen embrittlement during the compression testing of steels. It would appear that tensile stresses are required in order to cause this embrittlement.
9. The presence of hydrogen in steel changes the fracture type from that of a typically ductile metal to that of a typically brittle material.
10. The phenomenon of hydrogen embrittlement is dependent upon the treatment to which any given sample has been subjected. Steels are particularly susceptible if they are in either a hardened or a spheroidized condition. Cold working also increases the likelihood of hydrogen embrittlement (52).
11. The presence of hydrogen causes premature brittle fracture, under static loading conditions, in high strength alloy steels. This phenomenon is often referred to as "delayed failure" or "static fatigue." (51, 53, 54)

12. The presence of hydrogen in steel does not affect the metal in the unstrained condition. The removal of hydrogen from solid steel prior to straining ensures full ductility. It would appear that hydrogen embrittlement requires the presence of diffusible hydrogen during the course of the straining.
13. If the hydrogen concentration varies throughout a specimen, the hydrogen-rich areas will be those which are least ductile, and their premature fracture - during a tensile test - will result in an overall ductility of the specimen which is typical of that of the locally enriched areas, rather than the average hydrogen content.

Several theories have been proposed to account for the embrittlement of steels by hydrogen. Zapffe (55) proposed a mechanism based on Smith's (24) "rift" theory of solution in which high pressures were developed due to hydrogen in the "rift" networks. The hydrostatic forces developed were sufficient to spring the metal lattice apart. There are several shortcomings of this mechanism, one of the predominant ones being its inability to account for the absence of a hydrogen embrittlement effect in compression.

Petch (56) has proposed a mechanism based upon the absorption of hydrogen on the surfaces of microcracks in the steel and the subsequent reduction in the surface energy. This would reduce the amount of strain energy required to form a crack. Kazinczy (57) has suggested that the presence of gaseous hydrogen in the microcracks is the

important factor. The adiabatic expansion of this gas during the growth of the crack introduces an additional term into the expression for the amount of energy released. Thus, the critical stress required for crack propagation is lowered. These two theories account for several observed features of hydrogen embrittlement. However, both of these mechanisms depend on the diffusion of hydrogen to microcracks and hence would not predict that the degree of embrittlement would diminish as the temperature is increased above room temperature.

Vaughan and de Morton (58, 59) have proposed a mechanism based on a strain-hardening effect. It is suggested that the hydrogen is initially in interstitial solution but diffuses to the active slip planes under the influence of an applied stress. Here the hydrogen forms atmospheres which hinder the motion of dislocations. Some difficulty arises in explaining the observation (50) that hydrogen can suppress the yield point phenomena normally associated with carbon or nitrogen. Vaughan and de Morton suggest that this is due to the formation of hydrogen atmospheres, rather than carbon or nitrogen atmospheres, due to the greater interaction energy of the former. The lack of a yield point under these conditions implies that the hydrogen is able to diffuse rapidly enough to keep pace with the dislocations. This is contrary to their initial proposal that the embrittlement is due to the hydrogen impeding the motion of dislocations. Rogers (60) has presented evidence that the hydrogen atoms are less tightly bound by dislocations than are the carbon and nitrogen atoms. He suggests that hydrogen would not initially displace a significant number of

nitrogen or carbon atoms, but would attach itself to loops of dislocations that are freed from carbon or nitrogen by thermal fluctuations. This would lower the energy and hence the stress necessary for the formation of a critical-size loop. At room temperature, hydrogen could reduce the yield stress significantly and no yield point would be observed. As the temperature is reduced, the thermal motion of the dislocations would decrease and they would remain associated with their carbon and nitrogen atmospheres. Hence, a yield point would be observed at lower temperatures. These predictions were found experimentally to be true for Armco iron (60). This material, which normally shows a yield point at room temperature, was not found to exhibit a yield point at room temperature after charging with hydrogen. The yield point returned when the test temperature was decreased to -12°C and increased in magnitude with decreasing temperature. Internal friction studies also showed that the energy absorption peak associated with nitrogen in iron increased in amplitude only after the specimen was strained and not when the wire was charged with hydrogen. It can be justly concluded from these arguments that hydrogen embrittlement cannot be explained in terms of a strain-aging process.

The theory of hydrogen embrittlement in steels proposed by Troiano (61), although lacking at points for a clear physical mechanism, seems to account for all reliable experimental observations made to date. The failure process under the influence of hydrogen is divided into three stages.

1. The incubation period.

2. A period of relatively slow crack propagation.
3. Catastrophic failure with extremely rapid crack growth.

Just prior to testing, the hydrogen is uniformly distributed throughout the specimen. However, the application of a stress generates stress gradients and hence activity gradients which result in the diffusion of hydrogen to areas of high stress state. The cohesion of the lattice is reduced at these points and crack nuclei are formed. The propagation of these cracks depends upon the diffusion of a critical concentration of hydrogen to the advancing tip of the crack. This again is dependent upon the diffusion of hydrogen, and resistivity measurements have demonstrated the discontinuous nature and the temperature dependence of this process. The third stage occurs when the load-bearing area has been reduced by the propagation of cracks such that the fracture strength of the material is exceeded. Troiano speculates how hydrogen lowers the cohesive strength of the lattice. Several facts are used in his argument. Electrons of the hydrogen atoms in solution in a transition metal will enter the d bands of the metallic cores. In addition, the repulsive forces determining the interatomic distances of transition metals are due to the overlapping of their d bands. Thus, it may be expected that an increase of the electron concentration would produce an increase in the repulsive forces between the metallic cores, or, in other words, a decrease in the cohesive strength of the lattice. Also, the importance of repulsive forces between the ions increases when the d shell is almost full (62). There are several observations which support this hypothesis. The first is that thus far only transition

elements have been observed to be hydrogen embrittled. The electron concentrations of iron and chromium are less than that of nickel. Hence, additions of these elements to nickel should reduce the propensity of nickel for hydrogen embrittlement. This behavior has indeed been observed in iron-nickel alloys (63). A similar behavior should result from the addition of copper to nickel. The degree of embrittlement should increase with additions of copper and then decrease as the d band of nickel is progressively filled. This proposed behavior has also been observed experimentally (63).

It is interesting to note that in the mechanism proposed by Troiano for hydrogen embrittlement there is no aspect which limits the process to embrittlement by hydrogen. It is quite possible that carbon or other elements might behave in a similar manner if the temperature is raised to allow suitable diffusion rates. Scott and Troiano (64) have indeed shown that the behavior of a hot-work die steel containing 0.536 weight per cent carbon in the range of 700 to 1000°F is analogous to that of a hydrogen-containing steel around room temperature.

Another hydrogen-metal interaction that is of practical importance is the embrittlement of copper which contains cuprous oxide (65, 66). The hydrogen diffuses into the copper and reacts with the oxide to form steam, which expands and disrupts the copper. If this reaction occurs below the critical temperature of water (374°C), the pressure generated in the voids previously occupied by oxide particles is limited by the vapor pressure of water which is

approximately 1 ton/in.² at the critical point. Above the critical point, all the water can be converted to steam, and pressures of the order of 40 tons/in.² can result. As a result of these very high internal pressures, brittle premature service failures of commercially pure copper in hydrogen environments have occurred.

The hydrogen-induced mechanical property changes that have been discussed thus far all result in brittle failures of the metal. Another common feature is that, although the hydrogen may be absorbed by the metal during a high-temperature heat treatment, the embrittlement of the metal by hydrogen occurs only when the piece is near room temperature.

The mechanical behavior of metals in a hydrogen environment at elevated temperatures has not received much attention. Douglas (67) reported that the creep strength of Inconel was less in a hydrogen environment than in argon at 704 and 815°C. Klima et al. (68) studied the stress-rupture and fatigue properties of A-286 (Fe-25 Ni-15 Cr-2 Ti-1 Mn-1 Mo-4 Nb + Ta) at 649°C and Inconel 700 (45 Ni-30 Co-15 Cr-3 Al-2 Ti-3 Mo) and S-816 (20 Ni-4 Fe-43 Co-20 Cr-4 W-4 Mo) at 815°C in hydrogen and in air. They concluded that the fatigue properties were unaffected by hydrogen. It was also concluded that the stress-rupture life of the S-816 alloy was less in hydrogen than in air and that the properties of the other two materials were equivalent in both environments. The latter conclusion is based on no more than eleven tests at a single stress level for each material. The maximum rupture life was 340 hours.

Kolgatin et al. (69) reported that tubular specimens of low and medium alloy steels pressurized with hydrogen demonstrated up to 40 per cent lower rupture strengths than specimens pressurized with nitrogen. A high alloy steel (Fe-17.25 Cr-10.35 Ni) showed reductions in rupture strength of up to 20 per cent at the same test conditions. The test temperature for both series of tests was 593°C and rupture lives of up to 10,000 hours were encountered. The possibility of strengthening due to nitrogen absorption was not considered. Hence, the literature concerning the mechanical behavior of metals in hydrogen at elevated temperatures is very limited.

CHAPTER III

EXPERIMENTAL DETAILS

I. CREEP-RUPTURE TESTS

In order to control the environment of a specimen during a high-temperature creep-rupture test, the test chamber shown in Figure 4 was utilized. The test chamber is made of type 310 stainless steel and is heated externally by a Nichrome-wire heating element. The joint between the extension rod and the test chamber is made with U-cup pressure-vacuum seals. These seals make it possible to maintain vacuum or pressure within the test chamber and yet not cause significant resistance to movement of the extension rods. Water jackets are provided at both the top and bottom of the chamber to cool the seals. Two Chromel-P/Alumel thermocouples are brought through a seal at the top of the chamber and attached to the gage section of the test specimen. Another thermocouple is placed in a well for use as a control thermocouple in case the test environment adversely affects the thermocouples inside the chamber.

In order to minimize the effects which a particular environment may have upon the properties of a specimen by exposure before the stress is applied, all tests are heated to temperature under a vacuum of less than 1×10^{-4} torr. Small sheets of zirconium are suspended near the specimen to help remove oxidizing impurities. After reaching the test temperature, the argon or hydrogen environment is admitted. The hydrogen

Figure 4. Chamber for environmental stress-rupture tests at elevated temperatures.

is previously passed through a purification train consisting of a Deoxo unit for removing oxidizable impurities and Drierite for removing water vapor. A flow rate of $0.5 \text{ ft}^3/\text{hr}$ (STP) is maintained through the chamber. Tests in argon are run by slightly different procedures. Normally, the chamber is charged with argon (to a pressure of 10 pounds per square inch, gage) and sealed for the duration of the test. If the gas pressure decreases with time, the test is discontinued and the test results are not considered. An alternate procedure for testing in argon involves the use of a dynamic argon environment. The argon is passed over Drierite and columbium turnings at 800°C for purification.

II. TEST MATERIALS

This study involves several test materials ranging from high purity metals to complex commercial alloys. The designations given to each material are given in Table II, and further details concerning chemical composition and vendor are given in the Appendix.

Because of the various shapes and forms of the materials investigated, several types of specimens were used for mechanical property tests. The details of these specimens are given in Figure 5. A special type of test configuration was used for the zone-refined nickel due to its small initial diameter. The 0.250-in.-diameter rod was cut into 3-in. lengths and machined to a uniform diameter of 0.230 in. One-half inch on each end was coated with wax and the remaining 2 in. were chemically polished to 0.225 in. with a solution of 40 cm^3 nitric acid, 60 cm^3 acetic acid, and 0.50 cm^3 hydrochloric acid. One-inch-diameter molybdenum end

TABLE II
TEST MATERIALS

Material	Designation
Nickel 200	R-1031
Nickel 270	U. T.
Nickel 270	Heat 327
Nickel	Electron-beam zone-refined
Nickel	Electron-beam melted
Nickel	Nivac P
Copper	High purity
Type 304 Stainless Steel	R-1103
Iron	Electrolytic
Armco Iron	R-121
Inconel Alloy 600	R-892
Inconel Alloy 600	NX 892

Figure 5. Specimens used for mechanical property tests.

pieces were drilled to a depth of 0.50 in. so that the specimen was a slip fit. The end pieces and the specimens were assembled and heated for 1 hr at 1200°C in vacuum. Due to the greater thermal expansion of the nickel and the interdiffusion which occurred between the molybdenum and the nickel, an integral specimen was obtained suitable for creep testing.

III. PERMEABILITY EXPERIMENTS

The test apparatus used to study the rate of permeation of hydrogen through Inconel alloy 600 is shown in Figure 6. The Inconel alloy 600 rod was enclosed by a furnace. The inside circuit including the hole in the Inconel, the capillary tubing, the sampling bulb, and the vacuum gage was initially evacuated and sealed off. This portion of the apparatus had a volume of 13.0 cm³. Hydrogen was passed through the can surrounding the Inconel tube and the increase in pressure in the inside circuit was measured as a function of time. Argon was then passed through the can surrounding the Inconel tube and the decrease of pressure in the inside circuit was measured. A gas sample could be sealed off at any desired time.

IV. SURFACE ENERGY MEASUREMENTS AND THIN FOIL CREEP EXPERIMENTS

The zero creep (70) technique was used for attempting to measure the surface energy of nickel in argon and in hydrogen environments. This technique involves the measurement of the creep rate of small nickel wires at varying stresses at elevated temperatures. The procedure

Figure 6. Apparatus for studying gas permeability.

normally used is that of measuring the creep rates of several small wires having various weights attached. The present variation of this technique involved the measurement of the creep rate of a single wire under different stresses. The Ainsworth Recording Semi-Micro Balance shown in Figure 7 was used for this purpose. The balance normally records the weight change of a specimen attached to the left pan as it reacts with some gas. A furnace is located under the balance table. The weight change recorded is actually an electrical signal from the linear differential transformer indicated by A. As the beam tilts, the signal varies. The balance was modified so that a 3-in.-long wire creep specimen was suspended from the left pan by a 0.0625-in.-diameter nickel extension member. A bottom extension member was extended through the O-ring seal shown at B. This seal was made so that the total length of the specimen and its extension members could be changed. The desired stress was obtained by placing weights on the right pan and variations of up to 400 mg could be made remotely by use of the automatic weight change system inside the bell jar. The deformation of the specimens was recorded with 0.050-in. deformation being distributed over a 10-in. chart. The specimens were attached to the extension rods by first slotting the rods, then inserting the wire in the slot, and finally spot welding the assembly together.

The creep tests on nickel foils were run in the equipment just described. The test specimens were 0.060 in. wide $\times$ 0.0015 in. thick $\times$ 3 in. long. This geometry was chosen so that the specimens could be thinned for transmission electron microscopy studies.

UNCLASSIFIED
PHOTO 53206

Figure 7. Modified microbalance for surface energy and micro-creep experiments.

V. SINTERING STUDIES

The rate of sintering of nickel compacts was measured by use of a quartz dilatometer. The compacts were made by hydrostatically pressing -100 mesh carbonyl powder at a pressure of 30,000 pounds per square inch. The "as-pressed" dimensions of the compacts were 0.25-in. diameter $\times$ 2 in. long. The dilatometer was enclosed so that the sintering environment could be argon, vacuum, or hydrogen. A dial gage with an accuracy of 0.0001 in. was enclosed in a bell jar and indicated the position of the quartz extension rod.

VI. DIFFUSION EXPERIMENTS

Three different types of diffusion experiments were run, each involving a different procedure. One diffusion experiment was concerned with measuring the rate of diffusion of cobalt-60 in nickel. The nickel used in this work was designated as Nivac P. Small specimens having the geometry shown in Figure 8 were machined from this material. They were annealed 1 hr in vacuum at 1300°C. The large end of the specimen was prepared metallographically to obtain a flat scratch-free surface for plating.

The cobalt-60 was obtained in the form of $\text{Co}^{60}\text{Cl}_2$ solution. Two millicuries of this solution were diluted with 60 milliliters of H_2O and used as the plating solution. The cathode was platinum and the nickel specimen was the anode. A direct-current potential of 6 volts was used, which resulted in a current flow of 9 milliamperes. The large end of the

UNCLASSIFIED
ORNL-LR-DWG 67232

Figure 8. Geometry of diffusion specimen.

specimen was touched to the surface of the plating solution, the circuit was made, and the specimen plated for 1 min. Surface activities of the order of 4000 counts per second (1.10 to 1.40 million electron volts) resulted.

The diffusion anneals were carried out in a tube furnace in which two 1 1/4-in. outside-diameter alumina tubes were placed. These tubes were placed symmetrically inside the 2 1/2-in. inside-diameter furnace tube to ensure the same temperatures within each of the smaller tubes. Argon was passed through one tube and hydrogen through the other. The argon was initially of 99.95 per cent purity and was further purified by passing it over columbium turnings at 800°C. The hydrogen was purified by drying with subsequent diffusion through a thimble made of Pd-10 weight per cent Ag. Flow rates of 0.025 cubic feet per hour (11.8 cm³ per min) were used for both gases. The temperature was measured with Pt₉₀Rh₁₀/Pt thermocouples which were attached with nickel wires to the small-diameter portion of the specimen. All thermocouples were calibrated before use by comparing them with a standard. The furnace temperature was controlled to within ±1.5°C during the diffusion anneal. The temperatures of the two specimens, one in each tube, always compared to within 1°C.

After the diffusion anneals, each specimen was aligned in a lathe so the surface on which the cobalt-60 was originally plated was normal to the lathe axis. The diameter of each specimen was reduced by machining from 0.750 to 0.500 in. to remove effects of possible surface diffusion. The diameters of each argon-hydrogen pair were machined to the same measurement.

Uniform layers, 0.002 in. thick, were then machined from the original interface. The chips were collected in a plastic box which enclosed the specimen and lathe collet. The section thicknesses were calculated from the weights of the chips as determined by a semimicrobalance.

The cobalt-60 activity of each section was determined using a 3-in. $\times$ 3-in. NaI(Tl) scintillation crystal enclosed in a 3-in.-thick lead chamber and a single-channel analyzer. The cobalt-60 decays to metastable nickel-60, giving a 1.17 million electron volts gamma; the metastable nickel-60 decays by isomeric transition to stable nickel-60, giving a 1.33 million electron volts gamma. The activity was determined between 1.10 and 1.40 million electron volts, which included both the 1.17- and 1.33-million electron volts gamma peaks associated with the cobalt-60 decay. The specific activity for each section was determined by dividing the activity by the section weight.

Another type of diffusion experiment involved a study of the voids formed during the interdiffusion of iron and nickel. The nickel used was taken from the lot designated as Nivac P, and the iron was from a small electron-beam melted slab. The latter material was not analyzed chemically. Specimens of the two materials were polished on metallographic paper and a nylon cloth using Linde B abrasive. The two polished surfaces were placed together, and the specimens were tightened in the molybdenum fixture shown in Figure 9. A tightening torque of 125 in.-lb was used. This initial compressive force and the additional force obtained due to the greater thermal expansion of nickel gave good

Y-37170

Figure 9. Compression fixture for diffusion couples.

bonding during a 1-hr anneal in vacuum at 600°C. The iron-nickel couple was then removed from the molybdenum fixture. Pairs of these specimens were run in the double tube furnace described previously with one specimen in argon and the other in hydrogen. After annealing, the specimens were cut so that the diffusion interface could be examined metallographically.

A third type of diffusion experiment was concerned with comparing the diffusion rates of carbon in nickel when the material was in argon and hydrogen environments. Nickel 270-UT was used in this experiment. Disks of this material were machined having dimensions of 0.75-in. diameter $\times$ 0.25 in. thick. These specimens were annealed 1 hr at 600°C and 1 hr at 1350°C in vacuum which gave an average grain size of 0.05 cm. This anneal was used because it was found that the 1-hr anneal at 1350°C alone resulted in the formation of grain boundary voids. These specimens were attached to a wire framework and inserted in a 1 1/2-in. inside-diameter stainless steel tube. A carburizing compound consisting of 50 grams of powdered graphite and 10 grams of BaCO_3 which contained 40 millicuries of isotopic carbon-14 was poured into the tube. An end cap was welded on and this tube was sealed inside a larger stainless steel pipe. The entire assembly was annealed for 170 hr at 900°C. The capsule was then opened and the specimens removed and cleaned. They were again annealed 1 hr at 1350°C to distribute the carbon homogeneously. This procedure had previously been found to result in a carbon content of 0.083 weight per cent. The specimens were run over standard metallographic papers and flattened by rubbing them over a flat steel

plate coated with diamond abrasive. Diamond particle sizes of 0.50 and 6 microns were used. The abrading was continued until the surfaces were flat to within 0.000023 of an inch, as determined by a helium monochromatic light source. Additional samples of the same material were prepared in an identical manner with the exception of the carburization treatment. These specimens had a reduced section similar to the specimens shown in Figure 8, page 43, except that the two longitudinal dimensions were each 0.250 in. instead of 0.500 in.

Pairs of the two types of specimens were used to make a diffusion couple. The flat sides were placed together and the couple was tightened in the molybdenum fixture shown in Figure 9, page 46. A torque wrench was used to tighten the molybdenum bolt so that a reproducible torque of 125 in.-lb was obtained. A thermocouple was attached directly to the assembly during the diffusion anneal.

At the conclusion of the diffusion anneal, the specimens were machined to a uniform diameter of 0.500 in. to remove any surface effects. Since carbon-14 emits a relatively weak beta particle (0.155 million electron volts) which is easily shielded, the technique of surface counting was adopted rather than counting a bulk sample. That is, a layer was machined from the specimen and the activity of the surface of the remaining specimen was counted rather than counting the activity in the section removed. The section thicknesses were determined by collecting and weighing the machined chips. A special counting jig was developed which fits in the tail stock of a lathe so that the surface activity could be measured without removing the

specimen. This apparatus is shown in Figure 10. An Anton G.M. tube with a window density of 1 milligram per square centimeter and a 64 scaler were used for detection and counting. The end window was covered by an aluminum disk having an opening of 0.125 in. To make a surface count, the counting assembly was moved close to the specimen surface. The bolt at A was loosened and the aluminum disk in front of the G.M. tube was pushed against the specimen face. This procedure gave a reproducible counting geometry.

Two notable sources of error existed in these measurements. The largest error was in the counting. Since the counting tube was shielded only by its metal body, the background count rate was quite high, approximately 200 counts per minute. A standard counting time of 5 min was used for making a surface activity measurement. As the specimen activity decreased, the background counts which had to be subtracted became almost equal to the total counts obtained while a surface activity measurement was being made. Thus the counting accuracy decreases as the specimen activity decreases. Another source of error was the tendency for whole grains to pull out while a thin section was being attempted. This was particularly troublesome in the carburized specimens.

VII. METALLOGRAPHIC TECHNIQUES

All specimens were mounted in Hysol thermosetting plastic. After the plastic had hardened sufficiently, the specimens were run over a series of metallographic papers consisting of 320, 400, and 600 grit.

Figure 10. Counting fixture for diffusion specimens.

Syntron vibratory polishing was used almost exclusively. Gamel and nylon polishing cloths were used with Linde A, Linde B, or diamond (0.50 micron) abrasive. If the material was soft, such as copper, the final polishing was done with a nylon cloth and diamond abrasive in order to preserve the edges of voids and cracks which were present in the specimens. The polishing of harder materials was concluded on a Gamel cloth with Linde B abrasive. Fairly standard metallographic etchants were used in most cases and these will be indicated on the individual photomicrographs.

The only material which was prepared in a somewhat unorthodox manner was nickel. This material is quite soft and polishing normally causes the metal to flow over the scratches and leave the appearance of a well-polished surface. However, etching removes this smooth surface layer and reveals the scratches. A technique was developed for chemically polishing this material. After the specimens were run over the metallographic papers, they were run for a short time on a Gamel cloth with Linde A abrasive. They were then swabbed vigorously for 1 min while submerged in a solution of 70 cm³ acetic acid, 30 cm³ nitric acid, and 0.50 cm³ hydrochloric acid. This removes the surface layer and reveals the grain structure.

CHAPTER IV

EXPERIMENTAL RESULTS

Since this study was prompted by the experimental observation that the high-temperature creep strength of Inconel is inferior in a hydrogen environment as compared with its strength in an argon environment, a large portion of time has been spent in learning the characteristics of this environmental effect. This has been done by examining the creep properties of several materials in argon and hydrogen environments. These materials include two heats of commercial Inconel, Nickel 200, electron-beam zone-refined nickel, Nickel 270, high-purity copper, Armco iron, electrolytic iron, and type 304 stainless steel. In testing these materials, several variables were examined: test temperature, stress, grain size, carbon content, and cold working prior to testing. The results of tests on each material will be presented. Because of the intrinsic differences between supposedly "duplicate" test specimens, creep tests were run in which the same test specimen was used and the environment was cycled between argon and hydrogen.

Since the creep experiments and associated metallographic and chemical studies did not yield much information about the mechanism responsible for the different creep behavior in argon and in hydrogen environments, it was necessary to run several additional experiments. These experiments involve:

1. Examination of the tested specimen by x-ray diffraction to determine whether there were significant differences in substructure.
2. Measurements of the permeation rate of hydrogen through Inconel.
3. Measurements of the surface energy of nickel in argon and in hydrogen environments.
4. Comparison of the rates of sintering of nickel powder in argon and in hydrogen.
5. Comparison of the size and geometry of voids formed in nickel during the interdiffusion of iron and nickel in hydrogen and argon environments.
6. Measurements of the rate of diffusion of cobalt-60 in nickel.
7. Creep studies on thin nickel strips with subsequent electron transmission microscopy.
8. Comparison of the rates of diffusion of carbon in nickel in argon and hydrogen environments.

Although these experiments may seem unrelated at this point, it will be shown later that each experiment contributes something to our understanding of the mechanical behavior of metals in a hydrogen environment.

I. STRESS RUPTURE

Stress-Rupture Properties of Inconel Sheet - Heat NX892

The results of a series of creep tests at 815°C on Inconel sheet specimens are summarized in Table III. Two tensile tests were run at the same temperature, and the results of these tests are given in Table IV. The creep data are illustrated graphically to demonstrate several points. The actual creep curves plotted in Figure 11 show that the influence of hydrogen increases as the strain rate decreases. This point is also illustrated by the stress-rupture plot in Figure 12. For rupture lives of 200 hr or less, the influence of hydrogen is negligible; whereas, the rupture life in hydrogen is less by a factor of about three when the rupture life in argon is 2000 hr. This reduction in the rupture life in hydrogen results from a higher minimum creep rate. This is illustrated by Figure 13 where the logarithm of the minimum creep rate is plotted against the logarithm of the rupture life. Some difficulty was encountered in determining the minimum creep rate since this material did not exhibit the normal, linear, secondary creep stage from which the minimum creep rate is normally taken. In these tests a separate graph was made which showed in detail the initial portion of each creep curve. The minimum creep rate was determined by drawing a tangent to this curve. No detectable influence of hydrogen on the rupture ductility has been observed. This conclusion follows from Figure 14. Another interesting correlation is shown in Figure 15 where the logarithm of the rupture life is plotted against the logarithm

TABLE III

SUMMARY OF STRESS-RUPTURE DATA ON INCONEL SHEET

Material Designation: NX892

Specimen Geometry: 0.125-in.-thick sheet ×

Condition of Material: As-received

2.50-in.-long gage

Test Temperature: 815°C

section

Test No.	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Minimum Creep Rate (%/hr)	Hardness ^a after Test (DPH)	Average ^b Carbon Content after Test (wt %)	Reduction in Rupture Life due to Hydrogen (%)
972	10,000	Argon	24.0	42.2	1.19	129.3 (118.9-141.9)		
948	10,000	Hydrogen	26.4	53.2	0.972	124.8 (103.3-143.2)		
985	7,670	Argon	75.5	25.0	0.276			
970	7,500	Hydrogen	79.7	32.6	0.253			
1212	6,000	Argon	260.0	29.7	0.0810	114.1 (99.1-125.4)		} 23.1
1218	6,000	Hydrogen	200.3	26.6	0.0875	115.3 (103.3-128.1)		
1143	5,000	Argon	450.0	25.0	0.0323	105.2 (76.1-121.6)	0.017	} 20.0
1215	5,000	Hydrogen	360.0	28.2	0.0383	111.7 (103.3-118.9)	0.014	
906	3,500	Argon	2168.7	15.6	0.00225	103.7 (95.3-111.6)	0.034	} 62.0
1141	3,500	Hydrogen	825.0	14.1	0.00597	102.1 (90.9-114.6)	0.011	

^aAverage and range given are based on eight readings made 0.050 in. apart.^bAverage carbon content of the as-received material was 0.076 wt %. Individual determinations were 0.13, 0.06, and 0.04 wt %.

TABLE IV

SUMMARY OF TENSILE TESTS ON INCONEL SHEET

Material Designation: NX892
 Specimen Geometry: 0.125-in.-thick sheet x
 2.50-in.-long gage section
 Condition of Material: As-received
 Test Temperature: 815°C
 Strain Rate: 2.5%/min

Environ- ment	Yield Strength (psi)	Ultimate Strength (psi)	Elongation (%)	Hardness ^a after Test (DPH)
Argon	18,900	21,100	77.5	147.5 (140.7-155.2)
Hydrogen	18,100	20,300	66.0	150.7 (127.3-166.3)

^a Average and range given are based on eight readings made 0.050 in. apart.

Figure 11. Creep curves of Inconel (NX892) at 815°C in argon and hydrogen environments.

Figure 12. Stress-rupture properties of Inconel at 815°C.

Figure 13. Creep rate of Inconel sheet (NX892) in argon and hydrogen environments.

Figure 14. Rupture ductility of Inconel sheet (NX892) specimens tested in argon and hydrogen environments.

Figure 15. Correlation of strain rate and rupture life for Inconel sheet (NX892) tested in argon and hydrogen environments.

of the minimum creep rate. Machlin (16) predicted that these variables should correlate for cases where the measured creep rate and the creep rate producing vacancies for the voids are the same. The important point to be made from Figure 15, page 61, is that, if two specimens (one in an argon environment and the other in hydrogen) developed the same minimum creep rate, the rupture lives of both specimens would be predicted to be equivalent. However, the stress required to produce equivalent minimum creep rates in the two environments may differ considerably.

Several of the specimens were analyzed for carbon after the creep tests to determine whether significant loss of carbon had occurred. These results, which are given in Table III, page 55, are inconclusive. There seems to be some loss of carbon in specimens tested in argon as well as in hydrogen. However, the scatter obtained in carbon analyses of the as-received material makes a conclusion difficult.

Hardness measurements were also made to determine whether this property was significantly altered by the hydrogen. Eight readings were taken 1 in. from the fracture on a mounted longitudinal section of each specimen. These measurements are given in Tables III and IV, pages 55 and 56, respectively. The hardness continued to decrease with increasing test time but was not significantly different in a pair of specimens run in argon and in hydrogen at equivalent stress levels. The reason for this decrease in hardness may have been decarburization or it may have been that impurities agglomerated (possibly

in grain boundaries) into coarse precipitates with time and contributed less to the microhardness as measured in the center of a grain.

All of the specimens tested were examined metallographically. The photomicrographs in Figures 16 through 23 illustrate the findings of this study. All of the fractures were intergranular at 815°C, as would be expected. The photomicrographs, unless specified otherwise, were taken 0.25 in. from the fracture. The specimen tested in a conventional tensile test at a strain rate of 2.5 per cent per hour (Figure 16) recrystallized in some areas near the fracture. The cracks formed were elongated due to the high strain the specimen underwent. A similar type of microstructure was observed in the specimen tested in a creep test at 10,000 pounds per square inch (Figure 17). The specimen tested at 6000 pounds per square inch (Figure 18) recrystallized only in very small areas. The cracks principally were normal to the applied stress. At 5000 pounds per square inch, the cracks formed were considerably smaller and most were oriented normal to the applied stress (Figures 19 and 20). Figures 21 and 22 illustrate the fact that the cracks formed while testing at low strain rates were distributed uniformly throughout the specimen. The area shown in Figure 22 is located 1 in. from the fracture where the specimen width increases from 0.25 to 0.75 in. Even in this area, a large number of cracks are present. Crack formation was noted to occur more uniformly as the strain rate (or stress) decreased. The cracks at the low strain rates also are generally quite small and appear in many cases to be composed of small voids joined together. Figures 19 and 20 and 21 and 23

Y-41447

Figure 16. Photomicrograph of Inconel (NX892) tested in tension at 815°C at a strain rate of 2.5 per cent per hour. Environment was argon. Located 0.25 in. from fracture. Etchant: aqua regia. 100x.

Y-41450

Figure 17. Photomicrograph of Inconel (NX892) tested at 10,000 pounds per square inch in argon at 815°C. Test 972. Located 0.25 in. from fracture. Etchant: aqua regia. 100x.

Y-41455

Figure 18. Photomicrograph of Inconel (NX892) tested at 6000 pounds per square inch in argon at 815°C. Test 1212. Located 0.25 in. from fracture. Etchant: aqua regia. 100x.

Y-41466

Figure 19. Photomicrograph of Inconel (NX892) tested at 5000 pounds per square inch in argon at 815°C. Test 1143. Located 0.25 in. from fracture. Etchant: aqua regia. 100X.

Y-41470

Figure 20. Photomicrograph of Inconel (NX892) tested at 5000 pounds per square inch in hydrogen at 815°C. Test 1215. Located 0.25 in. from fracture. Etchant: aqua regia. 100X.

Y-41461

Figure 21. Photomicrograph of Inconel (NX892) tested at 3500 pounds per square inch in argon at 815°C. Test 906. Located 0.25 in. from fracture. Etchant: aqua regia. 100X.

Y-41596

Figure 22. Photomicrograph of Inconel (NX892) tested at 3500 pounds per square inch in argon at 815°C. Test 906. Located 1 in. from fracture. Etchant: aqua regia. 100x.

Y-41458

Figure 23. Photomicrograph of Inconel (NX892) tested at 3500 pounds per square inch in hydrogen at 815°C. Test 1141. Located 0.25 in. from fracture. Etchant: aqua regia. 100x.

compare the appearances of pairs of specimens tested at equivalent stresses in argon and in hydrogen. These photomicrographs do not reveal any striking differences in the distribution, size, or geometry of cracks formed in the two environments.

An attempt was made to determine by a somewhat more refined technique whether there were significant differences in the number or size of cracks in specimens tested in argon and in hydrogen. The procedure used was that of placing the mounted specimen on the stage of a microhardness tester so that one side of the specimen was parallel to the direction of motion of the stage. As the stage was moved, the cracks were counted and their size determined by the micrometer used to position the stage. The results of this study are summarized in Table V. The accuracy of the measurements was ± 0.0001 in. so there is no conclusive difference in the average size of the cracks formed in the two environments. The first two pairs of specimens seem to contain a larger number of cracks in the specimens tested in argon. However, the last pair of specimens indicates the opposite trend. In light of this inconsistency and the variations obtained in independent traverses along different parts of the specimens, it is concluded that these results do not demonstrate any consistent differences between specimens tested in argon and in hydrogen.

Stress-Rupture Properties of Inconel Rod - Heat R-892

The results obtained from several tests on Inconel rod are summarized in Table VI. Three tensile tests were also run and the

TABLE V

CRACK MEASUREMENTS ON INCONEL SHEET

Material Designation: NX892
 Specimen Geometry: 0.125-in.-thick sheet x
 2.50-in.-long gage section
 Condition of Material: As-received
 Test Temperature: 815°C

Test No.	Stress (psi)	Environment	Rupture Life (hr)	Length Traversed (in.)	Location of Traverse	Number of Cracks	Cracks per Inch	Total Width of Cracks (in.)	Average Crack Width (in.)
1212	6000	Argon	260.0	0.6564	center	68	104	0.0290	0.00043
				0.6539	side	76	116	0.0342	0.00045
1218	6000	Hydrogen	200.3	0.7629	center	59	77	0.0187	0.00032
1143	5000	Argon	450.0	0.6974	center	94	135	0.0397	0.00042
				0.7004	side	105	150	0.0520	0.00050
1215	5000	Hydrogen	360.0	0.7199	center	65	90	0.0264	0.00041
906	3500	Argon	2168.7	0.7155	center	53	74	0.0217	0.00041
				0.7302	side	80	110	0.0412	0.00052
1141	3500	Hydrogen	825.0	0.7699	center	97	126	0.0310	0.00032
				0.7489	side	71	95	0.0144	0.00020

TABLE VI

SUMMARY OF CREEP DATA ON INCONEL ROD

Material Designation: R-892
 Specimen Geometry: 0.250- or 0.375-in.-diameter x
 2.50-in.-long gage section
 Condition of Material: As-received

Test No.	Specimen Diameter (in.)	Temp (°C)	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)	After-Test ^a Carbon Analysis (wt %)	Reduction in Rupture Life due to Hydrogen (%)
1426	0.250	704	20,000	Argon	25.6	70.0	75.0	1.13		
1371	0.250	704	20,000	Hydrogen	17.6	67.5	62.6	1.98		} 31.3
1427	0.250	704	10,000	Argon	728.6	50.0	53.2	0.0334		} 7.9
1373	0.250	704	10,000	Hydrogen	670.7	60.0	62.1	0.0360		
1522	0.250	704	8,500	Argon	1260.6	46.1	47.6	0.0163		
1676	0.250	704	8,500	Hydrogen	1110.2	48.8	44.6	0.0169		} 11.9
1129	0.375	815	10,000	Argon	13.6	72.5	71.27	2.50		
1115	0.375	815	10,000	Argon	15.7	70.0	72.96	2.54		
1127	0.375	815	10,000	Hydrogen	10.6	77.5	73.24	2.78		
1162	0.375	815	7,500	Argon	43.7	47.9	55.20	0.528		
1160	0.375	815	7,500	Hydrogen	41.6	47.9	56.61	0.620		} 4.8
1163	0.375	815	3,500	Argon	484.3	35.4	34.28	0.0287	0.065	
1161	0.375	815	3,500	Hydrogen	379.4	37.5	40.63	0.0203	0.096	} 21.7
1249	0.375	815	2,500	Argon	1314.0	51.3	36.0	0.0115		
1186	0.375	815	2,500	Hydrogen	933.7	40.0	28.09	0.0140	0.074	} 28.9
1551	0.250	927	3,500	Hydrogen	20.6	53.8	48.8	0.0640		
1385	0.250	927	2,000	Argon	84.1	58.8	39.1	0.325		
1344	0.250	927	2,000	Hydrogen	117.9	37.5	26.72	0.280	0.027	
1364	0.250	927	1,500	Argon	211.8	57.6	38.2	0.137		
1366	0.250	927	1,000	Argon	840.7	63.1	34.3	0.0445		

^aCarbon content of as-received material was 0.05 wt %.

results of these tests are given in Table VII. Since the creep behavior at several temperatures was investigated, sufficient data were not obtained at each temperature to construct meaningful stress-rupture plots. The individual creep curves shown in Figure 24 were obtained at 704°C for the material in the as-received condition. The reduction in rupture life due to hydrogen increases as the strain rate or stress decreases. No effects of hydrogen on the ductility are discernible. The nonlinear creep curves obtained make creep-rate values rather arbitrary. However, it is obvious that hydrogen alters the entire creep curve and its influence is not confined to any particular creep period. Several creep curves obtained on the as-received material at 815°C are shown in Figure 25. The influence of hydrogen is qualitatively the same as that exhibited at the 704°C test temperature. The tests at 927°C were not as successful as the two series at the lower temperatures. Two major difficulties were encountered. The first was that Chromel-P/Alumel thermocouples seem to be adversely affected by hydrogen so that the temperature measurements were not reliable. This problem was aggravated by the fact that the thermocouples in the wells (which ordinarily could be changed) bonded to the well. A second difficulty was that the seals around the pull rods ran at such a high temperature that purity of the test environment was a problem. For these reasons, the results of the tests at 927°C are given in Table VI, page 74, but will not be considered further.

The main objective in running these tests at several temperatures was to determine how the influence of hydrogen varies with

TABLE VII

SUMMARY OF TENSILE TESTS ON INCONEL ROD

Material Designation: R-892
Specimen Geometry: 0.375-in.-diameter rod
Condition of Material: As-received
Test Temperature: 815°C
Strain Rate: 2.0%/min

Environ- ment	Yield Strength (psi)	Ultimate Strength (psi)	Elongation (%)	Reduction in Area (%)
Argon	19,740	21,550	79.0	96.0
Hydrogen	16,830	21,360	74.0	96.4
Hydrogen	19,220	21,785	72.5	96.0

Figure 24. Creep properties of Inconel (R-892) at 704°C.

Figure 25. Creep properties of Inconel (R-892) at 815°C.

temperature. Such a comparison is most correctly made in terms of the fractional decrease in the rupture life due to the presence of hydrogen. For tests 1522 and 1676, this quantity is 11.9 per cent. The pair of tests at 10,000 psi and 704°C (tests 1427 and 1373) exhibit a per cent reduction of 7.9. At 815°C the per cent reduction due to hydrogen is 21.7 for tests 1163 and 1161 and 28.9 for tests 1249 and 1186. Hence, hydrogen seems to exert a greater influence at 815°C than at 704°C.

Several tests were run to determine the influence of heat treatment on the magnitude of the hydrogen effect. The results of these tests are summarized in Table VIII and are presented graphically in Figure 26. Annealing Inconel at successively higher temperatures would be expected to increase its creep resistance due to increasing the grain size and putting additional carbon into solution. This was observed experimentally as can be seen by the results of tests 1491, 1554, and 1552. The rupture life of the material annealed 1 hr at 1204°C was a factor of seven greater than the material in the as-received condition. Although annealing significantly changed the rupture life, it did not significantly alter the influence of hydrogen. The pair of specimens tested in argon and in hydrogen in the as-received condition (tests 1491 and 1546) showed a reduction in rupture life due to hydrogen of 35.4 per cent. The pair annealed 1 hr at 1204°C (tests 1552 and 1572) exhibited a reduction of 31.9 per cent. Another variable included in the results described in Table VIII and in Figure 26 is carbon content. The specimens used in tests 1441 and

TABLE VIII

CREEP-RUPTURE DATA SHOWING THE EFFECT OF HEAT TREATMENT ON THE CREEP OF INCONEL (R-892)
AT 3500 PSI AND 815°C

Specimen Geometry: 0.250-in.-diameter rod

Test No.	Annealing Treatment	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)	After-Test ^a Carbon Content (wt %)	Reduction in Rupture Life due to Hydrogen (%)
1491	As-received	Argon	546.1	40.0	34.7	0.0236		} 35.4
1546	As-received	Hydrogen	352.9	31.3	30.1	0.0250		
1554	Anneal 1 hr at 1038°C in argon	Argon	632.1	48.7	36.8	0.0214		
1441	7 hr at 927°C in CO plus 1 hr at 1038°C in argon	Argon	614.1	40.0	31.5	0.018	0.124	} 30.7
1439	7 hr at 927°C in CO plus 1 hr at 1038°C in argon	Hydrogen	425.6	42.5	35.4	0.0358	0.088	
1552	Anneal 1 hr at 1204°C in argon	Argon	2409.9	10.0	8.61	0.0020		} 31.9
1572	Anneal 1 hr at 1204°C in argon	Hydrogen	1642.2	10.0	8.60	0.0025		

^aCarbon content of as-received material was 0.05 wt %.

Figure 26. Creep-rupture properties of Inconel (R-892) tested at 3500 pounds per square inch and 815°C.

1439 were carburized in CO and annealed 1 hr at 1038°C in argon prior to testing. This treatment did not significantly alter the creep behavior from that observed for material which had received only the anneal at 1038°C (test 1554). It is also significant that the per cent reduction in the rupture life of the carburized material due to hydrogen was 30.7 per cent (tests 1441 and 1439). Hence, it would appear that neither grain size (over the range of 0.002 to 0.020 cm) nor carbon content (over the range of 0.05 to 0.124 weight per cent) significantly alters the influence of hydrogen at 815°C.

Several specimens were analyzed after testing to determine whether significant changes in the carbon content had occurred. The results of these tests are given in Tables VI and VIII, pages 74 and 80, respectively. These values were obtained by analyzing a thin disk of material cut from the gage section of the tested specimen and thereby represent the average carbon content of the sample. These results are inconclusive for obvious reasons. Specimens 1249 and 1186 which were tested in argon and hydrogen, respectively, were sampled by taking turnings from a 1-in. segment of the gage length of the specimen. Four cuts, 0.010 in. thick, and three cuts, 0.015 in. thick, were taken from each sample using a molybdenum-tungsten cutting tool. These specimens were each analyzed and the results are shown in Figure 27. The point representing the analysis of a section is placed at the mid-point of each section. The specimen tested in hydrogen (test 1186) seems to have been decarburized to a depth of about 0.010 in. The cyclic behavior of the results for both specimens is difficult to

UNCLASSIFIED
ORNL-DWG 63-6430

Figure 27. Carbon distribution in tested Inconel specimens.

explain but probably bears some relation to the habits of the analytical chemist rather than the material.

Several of the test specimens were mounted and examined metallographically. The initial state of the material prior to testing is illustrated in Figure 28. The material appears to be recrystallized and free of cold work. The average grain diameter is approximately 0.002 cm. The grains are delineated by a fine grain boundary precipitation of carbides, characteristic of Inconel. Figures 29 and 30 illustrate the structure of the material after testing at 2500 pounds per square inch and 815°C in argon and hydrogen environments, respectively. In general, the grain size did not change significantly during the test in either environment. However, the grain size increased considerably in a layer about 0.010 in. thick at the surface of the specimen tested in hydrogen. This was probably due to the occurrence of some decarburization in the hydrogen environment which is in agreement with the analytical data shown in Figure 27, page 83, for these same specimens. The surface precipitation shown in Figure 30 has not been identified but was present in most of the specimens. The cracks formed in both specimens were quite large, many being as large as the grain dimensions. There is some tendency for the larger dimension of each crack to be aligned normal to the applied stress, but not to the extent observed for other materials. This is probably associated with the small grain size of this material.

Figure 31 shows the microstructure of a specimen tested at 2000 pounds per square inch and 927°C in hydrogen. Under these test

Y-52584

Figure 28. Photomicrograph of Inconel (R-892) in the as-received condition. Etchant: aqua regia. Microhardness: diamond pyramid hardness is 140.2 (136.4-145.5). 100x.

Y-52578

Figure 29. Photomicrograph of Inconel (R-892) tested at 2500 pounds per square inch in argon at 815°C. Test 1249. Located 0.75 in. from fracture. Etchant: aqua regia. 100x.

Y-52576

Y-52577

Figure 30. Inconel (R-892) tested at 2500 pounds per square inch in hydrogen at 815°C. Test 1186. Located 0.75 in. from fracture. Etchant: aqua regia. 100x. Reduced 5 per cent.

Y-52586

Y-52585

Figure 31. Inconel (R-892) tested at 2000 pounds per square inch in hydrogen at 927°C. Test 1344. Located 0.75 in. from fracture. Etchant: aqua regia. Microhardness: diamond pyramid hardness is 135.5 (133.6-136.8); edge hardness: diamond pyramid hardness is 105. 100x. Reduced 5 per cent.

conditions, the decarburized layer is approximately 0.020 in. This surface layer was found to be softer than the bulk of the specimen with diamond-pyramid hardness values of 105 and 135.5, respectively. The average grain size of the material was unaffected by the test. Numerous intergranular cracks were formed which exhibited a tendency to be oriented normal to the applied stress.

Figures 32 through 36 compare the microstructures obtained in material having various heat treatments followed by testing at 3500 pounds per square inch and 815°C. The microstructure shown in Figure 32 is from a specimen tested in the as-received condition. The microstructure is characterized by numerous cracks which tend to orient normal to the applied stress. The specimen shown in Figure 33 was annealed 1 hr at 1038°C in argon prior to testing. This anneal did not result in any significant change in grain size, and the microstructure obtained after testing is very similar to that of the as-received material after testing (Figure 32). The microstructures shown in Figures 34 and 35 are from specimens carburized in carbon dioxide and annealed 1 hr at 1038°C in argon prior to testing in argon and hydrogen environments. The density of carbide precipitate is somewhat greater in these specimens than in those of lower carbon content, but the general features of the microstructure are the same. The specimen tested in hydrogen (Figure 35) was apparently decarburized to a depth of about 0.010 in. The 1-hr anneal at 1204°C increased the grain diameter to approximately 0.020 in., as indicated by Figure 36. The cracks in these specimens were intergranular and long in the direction

Y-52579

Figure 32. Inconel (R-892) tested at 3500 pounds per square inch in argon at 815°C. Material tested in the as-received condition. Test 1491. Located 0.75 in. from fracture. Etchant: aqua regia. 100X.

Y-52581

Figure 33. Inconel (R-892) tested at 3500 pounds per square inch in argon at 815°C. Material annealed 1 hr at 1038°C prior to testing. Test 1554. Located 0.75 in. from fracture. Etchant: aqua regia. 100x.

Y-52587

Figure 34. Inconel (R-892) tested at 3500 pounds per square inch in argon at 815°C. Material carburized in CO and annealed 1 hr at 1038°C in argon prior to testing. Test 1441. Located 0.75 in. from fracture. Etchant: aqua regia. Microhardness: diamond pyramid hardness is 130.6 (126.4-134.7). 100x.

Y-52588

Figure 35. Inconel (R-892) tested at 3500 pounds per square inch in hydrogen at 815°C. Material carburized in CO and annealed 1 hr at 1038°C in argon prior to testing. Test 1439. Located 0.75 in. from fracture. Etchant: aqua regia. Microhardness: diamond pyramid hardness is 131.1 (125.4-133.6). 100×

Y-52582

Figure 36. Inconel (R-892) tested at 3500 pounds per square inch in argon at 815°C. Material annealed 1 hr at 1204°C in argon prior to testing. Test 1552. Located 0.75 in. from fracture. Etchant: aqua regia. 100x.

normal to the applied stress. The surface layer of large grains probably resulted from the loss of carbon during the high-temperature anneal.

Stress-Rupture Properties of Nickel 200 - Heat R-1031

Before discussing the results of tests on this material, some explanation is in order concerning a known source of error involved in these tests. The test material came from at least four rods which were specified as having come from the same heat. The results of several chemical analyses which are given in the Appendix show that the test specimens varied in composition more than would be expected had the material been from the same heat. The influence of these chemical variations is not known exactly, but is suspected of being responsible for much of the scatter in the experimental results.

Several tensile tests were run to compare the tensile properties of this material in argon and hydrogen environments. The results of these tests are summarized in Table IX. At the test conditions used, these results indicate that the tensile properties are equivalent in argon and hydrogen.

The creep behavior of this material was investigated over a large range of test conditions. Test results obtained from specimens which were given a 1-hr anneal at 815°C in vacuum prior to testing are given in Table X. The test results at 593, 704, and 815°C are also presented in Figure 37 in the form of a stress-rupture plot. From Figure 37 it is apparent that the rupture life of this material at 593°C

TABLE IX

SUMMARY OF TENSILE TESTS ON NICKEL 200 AT 815°C

Material Designation: R-1031
 Specimen Geometry: 0.375-in.-diameter rod and
 0.250-in.-diameter rod
 Condition of Material: Annealed 1 hr at 815°C
 in vacuum
 Strain Rate: 2.0%/min

Environ- ment	Yield Strength (psi)	Ultimate Strength (psi)	Elongation (%)	Reduction in Area (%)	Specimen Diameter (in.)
Argon	3560	8,800	72.6	98.0	0.375
Hydrogen	4380	11,100	81.0	99.4	0.375
Argon	4210	10,200	74.0	99.9	0.250
Argon	5550	12,700	70.0	99.4	0.250
Hydrogen	5260	9,780	75.0	99.9	0.250
Hydrogen	4560	10,700	74.2	99.5	0.250
Average Values					
Argon	4440	10,600	72.2	99.1	--
Hydrogen	4733	10,500	76.7	99.6	--

TABLE X

SUMMARY OF CREEP DATA ON NICKEL 200 ROD

Material Designation: R-1031
 Specimen Geometry: 0.375-in.-diameter rod
 Condition of Material: Annealed 1 hr at 815°C in vacuum

Test No.	Temp (°C)	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)	After-Test Carbon Content (wt %)	After-Test Sulfur Content (wt %)	Reduction in Rupture Life due to Hydrogen (%)
1633	704	11,000	Argon	9.3	76.3	75.1	2.70	0.042		} 40.5
1705	704	11,000	Hydrogen	5.53	71.3	95.4	4.08			
1634	704	10,000	Argon	19.5	66.3	87.1	1.22			} 41.8
1834	704	10,000	Hydrogen	11.35	70.0	90.1	2.09			
1452	704	7,500	Argon	121.9	72.5	71.5	0.190	0.051	0.0015	} 10.1
1451	704	7,500	Hydrogen	109.6	77.5	71.5	0.176	0.036	< 0.001	
1677	704	6,000	Hydrogen	231.1	58.8	52.6	0.0933			} 30.7
1409	704	5,000	Argon	823.0	42.5	33.0	0.0225	0.053	0.0012	
1408	704	5,000	Hydrogen	570.4	47.5	45.1	0.0295	0.034	< 0.0010	} 16.4
1720	704	4,000	Argon	1449.2	32.5	26.7	0.0122			
1741	704	4,000	Hydrogen	1211.7	31.3	24.0	0.0138			} 24.3
1476	704	3,500	Argon	2477.5	26.3	22.6	0.0050	0.041	0.0020	
1475	704	3,500	Hydrogen	1845.2	25.0	20.7	0.0066	0.028	0.0015	
1929	593	25,000	Argon	0.35	79.4	88.3	75.0			
1933	593	20,000	Hydrogen	2.9	69.5	87.2	13.4			
2074	593	15,000	Argon	71.1	71.8	71.4	0.420			
2255	593	11,500	Hydrogen	477.8	55.6	49.9	0.0553			
2271	593	11,290	Argon	852.1	43.1	37.3	0.0302			
2073	593	11,000	Argon	360.0	17.7	15.1	0.0215			
2573	593	9,000	Hydrogen	2015.1	41.5	40.4	0.0086			

TABLE X (continued)

Test No.	Temp (°C)	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)	After-Test Carbon Content (wt %)	After-Test Sulfur Content (wt %)	Reduction in Rupture Life due to Hydrogen (%)
1920	927	1,000	Argon	415.0	12.5	9.85	0.0163			
1996	927	424	Argon	2640.2 ^a	1.64	12.2	0.00036			
1248	815	5,000	Argon	7.9	56.3	98.4	1.45	0.047		} 19.0
1247	815	5,000	Hydrogen	6.4	68.8	99.4	1.91			
1635	815	3,500	Argon	94.7	51.3	43.1	0.210	0.041		} 40.5
1234	815	3,500	Hydrogen	56.3	60.41	87.0	0.318			
1276	815	2,500	Argon	272.8	45.00	44.3	0.0635			} 37.9
1275	815	2,500	Hydrogen	169.4	25.00	19.7	0.0830			
1350	815	2,000	Argon	414.2	25.00	23.5	0.0275	0.051		} max 31.0
1443	815	2,000	Argon	434.0	26.3	24.9	0.0263	0.054		
1349	815	2,000	Hydrogen	317.7	17.5	12.9	0.0325			} min 23.3
1440	815	2,000	Hydrogen	299.2	16.3	15.4	0.0398			
1486	815	1,400	Argon	1314.8	13.8	10.4	0.0100			} 43.1
1490	815	1,400	Hydrogen	747.8	11.3	13.9	0.0141			

^aDiscontinued before fracture.

Figure 37. Creep-rupture properties of Nickel 200 in argon and hydrogen environments.

is not significantly influenced by hydrogen until rupture lives of the order of 1000 hr are encountered. At 704 and 815°C hydrogen exerts an influence on the rupture life when it is as short as 10 hr. The data indicate that, for an approximate 1000-hr rupture life, the reduction in creep life due to hydrogen is 40 per cent at 593°C, 25 per cent at 704°C, and 40 per cent at 815°C. In view of the scatter of the experimental data and the limited tests in hydrogen at 593°C, the value at this temperature is not considered to be very accurate. Qualitatively, it seems that hydrogen exerts a greater influence at 815°C than at 704°C. The series of creep curves shown in Figure 38 for a test temperature of 704°C illustrate the important features of the hydrogen effect. Just as was found for Inconel, the minimum creep rate is increased by hydrogen, and the fracture ductility is not significantly altered. The fracture ductility in terms of the reduction in area at the fracture is plotted in Figure 39 as a function of the rupture life. The data obtained at 593 and 704°C are adequately represented by a single curve with the test environment having no detectable influence. The data obtained at 815°C are best represented by another curve, but again the test environment does not seem a significant factor.

In Figure 40 the rupture life is plotted as a function of the minimum creep rate. As predicted by Machlin (16), the data at all three temperatures are adequately described by a single line having a slope of approximately -1. Statistical analysis of the experimental data gave a value of -0.916 for the slope. However, the most important point is that the data representing tests in hydrogen and those

Figure 38. Creep of Nickel 200 in argon and hydrogen environments at 704°C.

Figure 39. Ductility of Nickel 200 tested in argon and hydrogen environments.

Figure 40. Creep properties of Nickel 200 (R-1031).

representing tests in argon normally lie along the same line. This indicates that the rupture lives of two specimens, one in an argon environment and the other in hydrogen, which are creeping at the same rate are identical.

The results of several tests to determine the influence of annealing treatment on the creep properties of this material are summarized in Table XI. The first group of tests, which compare 815 and 1038°C anneals, are illustrated in Figure 41. The creep curves of material annealed 1 hr at 815°C and tested at 815°C were consistently found to exhibit the unusual shapes shown for tests 1440 and 1443. The 1-hr anneal at 1038°C not only increased the creep strength of the material but also resulted in creep curves of more conventional appearance. Based on these tests, hydrogen exerts a slightly greater influence on the material receiving the higher anneal prior to testing. The second group of tests in Table XI illustrates the influence of a prior anneal in hydrogen on the creep behavior of Nickel 200. Again, the creep strength appears to be enhanced by the longer anneal and the influence of hydrogen becomes slightly greater. The most important point here is that the influence of hydrogen is not removed by a long anneal in hydrogen prior to testing. This implies that the influence of hydrogen does not occur through the removal of some impurity from the nickel by the hydrogen. If this were the case, the material annealed in hydrogen should have this impurity removed and would demonstrate the creep behavior characteristic of the material in hydrogen whether the test environment is hydrogen or argon.

TABLE XI

EFFECT OF PRETEST ANNEALING TEMPERATURE ON THE CREEP PROPERTIES OF NICKEL 200 AT 815°C

Test No.	Environment	Heat Treatment	Stress (psi)	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)	Reduction in Rupture Life due to Hydrogen (%)
1350	Argon	1 hr at 815°C in vacuum	2000	414.2	25.0	23.5	0.0275	max 31.0
1443	Argon	1 hr at 815°C in vacuum	2000	434.0	26.3	24.9	0.0263	
1349	Hydrogen	1 hr at 815°C in vacuum	2000	317.7	17.5	12.9	0.0325	min 23.3
1440	Hydrogen	1 hr at 815°C in vacuum	2000	299.2	16.3	15.4	0.0398	
1374	Argon	1 hr at 1038°C in vacuum	2000	676.2	17.0	12.4	0.0156	39.4
1348	Hydrogen	1 hr at 1038°C in vacuum	2000	410.0	15.0	13.4	0.0204	
1486	Argon	1 hr at 815°C in vacuum	1400	1314.8	13.8	10.4	0.0100	43.1
1490	Hydrogen	1 hr at 815°C in vacuum	1400	747.8	11.3	13.9	0.0141	
2125	Argon	208 hr at 815°C in hydrogen	1400	1745.6	8.75	7.25	0.0032	62.6
2123	Hydrogen	208 hr at 815°C in hydrogen	1400	853.6	4.38	5.65	0.0051	

UNCLASSIFIED
ORNL-DWG 63-6443

Figure 41. Influence of annealing temperature on the creep of Nickel 200 in argon and hydrogen environments.

A few tests were run to study the influence of cold working on the creep of nickel. The results of these tests are summarized in Table XII and shown graphically in Figure 42. The important feature indicated by these tests is that prestraining at room temperature tends to reduce the susceptibility of the material to the influence of hydrogen during a creep test at 3500 pounds per square inch and 704°C.

Several of the specimens were analyzed for carbon and for sulfur after testing. The results indicate that the concentrations of both elements were lower in the specimens tested in hydrogen than in those tested in argon. However, the uncertainty in the analysis of the as-received material makes a conclusion difficult.

Several of the test specimens were examined metallographically to learn more about the deformation processes in Nickel 200. Photomicrographs of the material after it was annealed 1 hr at 815 and 1038°C in vacuum are shown in Figures 43 and 44, respectively. The average grain diameter increased from 0.009 cm in the material annealed at 815°C to 0.020 cm in the material annealed at 1038°C.

Figures 45 through 49 are photomicrographs of the specimens from the series of tests at 704°C, illustrated in Figure 38, page 101. The microstructure of a specimen tested at 11,000 pounds per square inch in an argon environment is illustrated in Figure 45. The fracture at this strain rate was primarily intergranular with profuse crack formation occurring near the fracture. Some recrystallization is also evident near the fracture. The crack formation was restricted primarily to the area near the fracture although the specimen apparently

TABLE XII

EFFECT OF PRETREATMENT ON THE CREEP PROPERTIES OF NICKEL 200
AT 704°C AND 3500 PSI

Specimen Geometry: 0.375-in. diameter

Test No.	Environment	History	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)
1476	Argon	Annealed 1 hr at 815°C in vacuum	2477.5	26.3	22.6	0.0050
1475	Hydrogen	Annealed 1 hr at 815°C in vacuum	1845.2	25.0	20.7	0.0066
1983	Argon	As-received, strained 5%	1897.3 ^a	18.8	18.3	0.0076
1981	Hydrogen	As-received, strained 5%	1536.8 ^a	16.8	17.7	0.0080

^aDiscontinued prior to failure.

Figure 42. Influence of prestraining on the creep properties of Nickel 200 at 704°C and 3500 pounds per square inch.

Y-52673

Figure 43. Photomicrograph of Nickel 200 (R-1031) annealed 1 hr at 815°C in vacuum. Etchant: acetic, nitric, and hydrochloric acids. Hardness: diamond pyramid hardness is 68.3 (60.0-76.6). 100X.

Y-52672

Figure 44. Photomicrograph of Nickel 200 (R-1031) annealed 1 hr at 1038°C in vacuum. Etchant: acetic, nitric, and hydrochloric acids. Hardness: diamond pyramid hardness is 77.4 (75.7-78.9). 100x.

Y-52689

Y-44951

Figure 45. Nickel 200 (R-1031) tested at 11,000 pounds per square inch in argon at 704°C. Test 1633. Upper photograph taken approximately 0.75 in. from fracture. Lower photograph taken at fracture. Etchant: acetic, nitric, and hydrochloric acids. 100X. Reduced 8 per cent.

Y-52685

Y-52686

Figure 46. Nickel 200 (R-1031) tested at 5000 pounds per square inch in argon at 704°C. Test 1409. Upper photograph taken approximately 0.75 in. from fracture. Lower photograph taken at fracture. Etchant: acetic, nitric, and hydrochloric acids. 100X. Reduced 8 per cent.

Y-52682

Figure 47. Nickel 200 (R-1031) tested at 3500 pounds per square inch in argon at 704°C. Test 1476. Photograph taken at fracture. Etchant: acetic, nitric, and hydrochloric acids. 100x.

Y-52681

Y-52680

Figure 48. Nickel 200 (R-1031) tested at 3500 pounds per square inch in argon at 704°C. Test 1476. Upper photograph taken near center of specimen 0.75 in. from fracture. Lower photograph taken at the edge of specimen approximately 0.75 in. from fracture. Etchant: acetic, nitric, and hydrochloric acids. 100x.

Figure 49. Nickel 200 (R-1031) tested at 3500 pounds per square inch in hydrogen at 704°C. Test 1475. Upper photograph taken near center of specimen 0.75 in. from fracture. Lower photograph taken at the edge of the specimen approximately 0.75 in. from fracture. Etchant: acetic, nitric, and hydrochloric acids. 100X. Reduced 8 per cent.

recrystallized throughout. No differences could be detected between the structure of this specimen and one tested in hydrogen at the same stress and temperature.

Representative photomicrographs of a specimen tested in argon at 5000 pounds per square inch and 704°C are shown in Figure 46, page 113. The fracture is intergranular with some recrystallization having occurred in this area. There is very little evidence of recrystallization away from the fracture. Deformation at this stress level leads to extensive grain boundary cracking. Some of these cracks are quite large, whereas others are small enough to have been formed by diffusional processes. Again, no differences between the microstructures of specimens tested in argon and hydrogen environments at this stress and temperature were evident.

The fracture of a specimen tested at 3500 pounds per square inch in argon at 704°C is shown in Figure 47, page 114. The cracking is extensive in this area with very little evidence of recrystallization. Photomicrographs taken 1 in. from the fracture area of this same specimen are shown in Figure 48, page 115. The deformation appeared to be quite inhomogeneous. Near the surface the grain size was quite large and numerous large grain boundary cracks were formed which seemed to originate at the surface. There was then a relatively dense area with only a few intergranular voids. In the interior the grain size was comparable with that of the as-annealed material and extensive grain boundary cracking and void formation occurred. The differences between the cracking near the surface and that in the interior of the specimen

can be rationalized in terms of the large grain size near the surface. This large grain size probably resulted from surface working as the specimens were being machined. The relatively dense area may have resulted from the diffusion of vacancies to the surface rather than condensing at potential void nuclei. In the center of the specimen, this competition for vacancies would not occur, and numerous voids would result. Figure 49, page 116, shows that the specimen tested in hydrogen at the same test conditions exhibited a similar structure. Hence, the type of structure obtained seems to be dependent upon the strain rate and not upon the test environment.

Figures 50 and 51 illustrate the structures of specimens which were prestrained 5 per cent and tested at 704°C and 3500 pounds per square inch in argon and hydrogen environments, respectively. Both of these tests were discontinued prior to failure so the cracking is not very extensive. It was found by using a special etchant that both specimens contained a substructure.

Figures 52 and 53 illustrate the influence of prior annealing treatment on the microstructure of Nickel 200 deformed at 815°C. Figure 52a shows a cross section of a specimen annealed 1 hr at 815°C in vacuum and tested at 815°C and 2000 pounds per square inch in hydrogen. The cracking is very inhomogeneous. Figure 52b shows the microstructure of this specimen. Considerable grain growth has occurred during the test. This gross change in grain size may account for the unusual shape of the creep curves obtained at 815°C. Figure 53a shows a specimen annealed 1 hr at 1038°C and tested at 815°C. The cracking

Y-52690

Y-47077

Figure 50. Nickel 200 (R-1031) tested at 3500 pounds per square inch in argon at 704°C. Material was strained 5 per cent prior to testing. Test 1983. Specimen etched with acetic, nitric, and hydrochloric acids for upper photograph. 100X. Specimen etched with 50 per cent KCN and 50 per cent $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to reveal substructure for lower photograph. 500X. Reduced 8 per cent.

Y-52691

Figure 51. Nickel 200 (R-1031) tested at 3500 pounds per square inch in hydrogen at 704°C. Material was strained 5 per cent prior to testing. Test 1981. Etchant: acetic, nitric, and hydrochloric acids. 100x.

Y-42444

a

Y-52676

b

Figure 52. Micrograph of sectioned Nickel 200 (R-1031) specimen tested at 2000 pounds per square inch in hydrogen at 815°C. Specimen annealed 1 hr at 815°C in vacuum prior to testing. Test 1349. Upper micrograph; 6X. Photomicrograph of specimen taken near the specimen edge about 0.75 in. from the fracture. Etchant: acetic, nitric, and hydrochloric acids. Lower photomicrograph; 100X.

Figure 53. Micrograph of sectioned Nickel 200 (R-1031) specimen tested at 2000 pounds per square inch in hydrogen at 815°C. Specimen annealed 1 hr at 1038°C in vacuum prior to testing. Test 1374. Upper micrograph; 6X. Photomicrograph of specimen taken near the specimen edge about 0.75 in. from the fracture. Etchant: acetic, nitric, and hydrochloric acids. Lower photomicrograph; 100X.

is more uniform in this specimen than in the one annealed at 815°C. The microstructure shown in Figure 53b, page 122, is characterized by grain boundary cracks and voids. No noticeable grain growth occurred during testing.

Creep Properties of Electron-Beam Zone-Refined Nickel

Test specimens of this material were run to compare their creep behavior in argon and in hydrogen environments. Due to the limited amount of test material available, only the seven tests listed in Table XIII were run. However, the results of these tests are quite significant and will be reviewed in detail. Tests 1727 and 1769 were the first tests run and it was necessary to increase the stress level several times to obtain failure in a reasonable time. However, the stress levels were changed on both tests at the same time so that the results would be comparable. The test in hydrogen failed in a significantly shorter time than did the specimen in argon. Two other polycrystalline specimens were tested under somewhat simpler stress conditions. The creep curves of these two tests are shown in Figure 54. The specimen in hydrogen failed after 656.5 hr, whereas the specimen in argon had not failed after 1345 hr. Representative microstructures of the specimen tested in hydrogen are shown in Figure 55. There is considerable evidence of recrystallization near the fracture. Numerous intergranular voids were formed throughout the specimen. As indicated in Figure 56, intergranular voids were also formed in the specimen tested in argon. Another feature which is similar in both specimens

TABLE XIII

SUMMARY OF TESTS RUN ON ELECTRON-BEAM ZONE-REFINED NICKEL

Specimen Geometry: 0.25-in.-diameter rod

(All specimens annealed 1 hr at 1200°C
in vacuum prior to testing)

Test No.	Temperature (°C)	Stress (psi)	Environment	Rupture Life (hr)	Strain at Rupture (%)
1727 ^a	815	1377	Argon	1389	--
		↓			
		2334			
1769 ^a	815	1377	Hydrogen	925	--
		↓			
		2086			
1998 ^a	815	2100	Argon	1345.1 ^b	0.95
1995 ^a	815	2100	Hydrogen	656.5	3.12
1688 ^c	815-927	--	Ar-H ₂	2472 ^b	22.7
			cycle		
1992 ^c	815	--	Ar-H ₂	1090 ^b	13.3
			cycle		
2209 ^c	600-815	--	Ar-H ₂	--	--
			cycle		

^a Polycrystalline.^b Test discontinued prior to failure.^c Single crystal.

Figure 54. Creep of electron-beam zone-refined nickel in argon and hydrogen at 2100 pounds per square inch and 815°C.

Figure 55. Nickel specimen tested at 2100 pounds per square inch in hydrogen at 815°C. Test 1995. Etchant: acetic, nitric, hydrochloric acids; 100X. Upper photograph - fracture; lower photograph - representative about 0.50 in. from fracture. Reduced 8 per cent.

Y-46853

Y-46854

Figure 56. Nickel specimen tested at 2100 pounds per square inch in argon at 815°C. Test 1998. Etchant: upper photograph - acetic, nitric, and hydrochloric acids; 100 $\times$; lower photograph - KCN and $(\text{NH}_4)_2\text{S}_2\text{O}_8$; 500 $\times$. Reduced 8 per cent.

is the substructure also represented in Figure 56, page 127. This was brought out by etching the specimens quite heavily in a 1:1 solution of potassium cyanide and ammonium persulfate.

Three single-crystal specimens of this material were tested under conditions where the test environment was alternated between argon and hydrogen. The creep results will be presented in Chapter IV, Section II, but some metallographic observations concerning these specimens will be presented at this point. A back-reflection x-ray pattern was taken of the crystal used in test 1688 before testing. It was found that the axis of the crystal did not correspond to any major direction but was oriented 5 degrees from the 210 direction and 4 degrees from the 320 direction. This specimen was subjected to various stresses over the temperature range of 815 to 927°C with a resulting deformation of 22.7 per cent. The specimen after test is shown in Figure 57. A back-reflection x-ray pattern was made on the deformed specimen. Considerable polygonization occurred during the test. However, the individual spots appear to be sharp, indicating little lattice distortion. A portion of the specimen was mounted and examined metallographically. Photomicrographs of the structure are shown in Figure 58. A few small grains were formed near the surface, but there is no increase in the number of voids present in this material. A piece of the as-received material is shown in Figure 59. The void concentration was fairly high in this material, probably due to gas evolution during the zone refining. As illustrated in Figure 58, it was possible to reveal the substructure in the tested specimen by

Y-45208

Figure 57. Nickel specimen from test 1688.

Y-46847

Y-46848

Figure 58. Nickel tested over the temperature range of 815–927°C under creep conditions in alternating argon and hydrogen. Test 1688. Etchant: upper photograph – acetic, nitric, and hydrochloric acids; 100×; lower photograph – KCN and $(\text{NH}_4)_2\text{S}_2\text{O}_8$; 500×.

Y-46851

Figure 59. Electron-beam zone-refined nickel in the as-received condition. Etchant: acetic, nitric, and hydrochloric acids. 100X.

using the KCN etchant. The substructure was more prevalent near the specimen surface. A vacuum fusion analysis was run on the specimen from test 1688 which gave the results: (1) oxygen about 21 parts per million, (2) nitrogen less than 5 parts per million, and (3) hydrogen about 11 parts per million. [Values before test were: (1) oxygen about 54 parts per million, (2) nitrogen less than 5 parts per million, and (3) hydrogen about 3 parts per million.] Hence, no significant changes occurred in the analysis of the material during the test.

The specimen used in test 1992 was subjected to an analysis similar to that just described. An x-ray pattern made before the test indicated that the specimen axis was approximately the same as that of the specimen used in test 1688. A pattern made after the test indicated that the material had polygonized and that the specimen axis had rotated approximately 5 degrees. Metallographic examination showed that the void concentration of the specimen had not increased as a result of the 13.3 per cent deformation under creep conditions. As indicated in Figure 60, a very pronounced substructure was revealed near the surface by etching.

Stress-Rupture Properties of Nickel 270

Several tests were run to evaluate the creep properties of Nickel 270 in argon and hydrogen environments. The results of these tests are presented in Table XIV. Figure 61 shows the same data in the form of a stress-rupture-life graph from which it is obvious that this material has a much shorter rupture life in hydrogen than in argon.

Y-46849

Figure 60. Nickel tested at 815°C under creep conditions in alternating argon and hydrogen environments. Test 1992. Specimen etched in 1:1 KCN and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. 100X.

TABLE XIV

SUMMARY OF CREEP DATA ON NICKEL 270 ROD

Specimen Geometry: 0.250-in.-diameter rod
 Temperature: 800°C
 Material Designation: Nickel 270
 Condition of Material: As-received

Test No.	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)	Reduction in Rupture Life Due to Hydrogen (%)
2766	2000	Argon	39.4	4.7	2.5	4.0×10^{-2}	
2719	1500	Hydrogen	14.6	1.6	1.6	3.6×10^{-2}	
2831	1250	Argon	156.7	4.7	2.0	9.0×10^{-3}	} 82.8
2823	1250	Hydrogen	26.9	4.7	1.2	4.0×10^{-2}	
2612	1000	Argon	381.4	1.6	2.2	1.6×10^{-3}	} 85.4
2440	1000	Hydrogen	55.6		1.2	1.3×10^{-2}	
2666	700	Argon	1411.7	1.1	1.2	9.3×10^{-4}	} 87.9
2578	700	Hydrogen	170.7	3.9	1.0	4.4×10^{-3}	
2424	500	Hydrogen	752.9	4.7	1.2	1.1×10^{-3}

Figure 61. Rupture life of Nickel 270 at 800°C.

Figure 62 shows that the minimum creep rate is accelerated by the presence of a hydrogen environment. The rupture strains are quite low for this material under all test conditions, and there does not seem to be any influence of environment on ductility. The influence of hydrogen on this material does not seem to be very dependent upon the strain rate. The per cent decrease in rupture life due to hydrogen was approximately 85 per cent over the entire range of strain rates investigated.

Several specimens were examined metallographically. A representative photomicrograph of the as-received material is shown in Figure 63. The structure appears quite clean with an average grain diameter of approximately 0.0004 cm. The microstructure of the same material after a 1-hr anneal at 800°C is shown in Figure 64. The grain size has increased by about a factor of ten. Figure 65 illustrates the microstructure of the Nickel 270 after creep testing at 1000 pounds per square inch in hydrogen. This photograph was taken near the fracture with the specimen in the unetched condition and illustrates the numerous grain boundary voids that were present. Figure 66 is a photomicrograph of the same specimen in the etched condition. The grain boundary voids are present throughout the specimen. The dark spots in the specimen are pits due to the concentration of HCl in the etchant being too high. The grain size is slightly larger than that of the specimen shown in Figure 64 that had been annealed 1 hr at 800°C. Hence, the grain size must stabilize rather quickly at the 800°C test temperature. Figure 67 shows the microstructure of a specimen tested

Figure 62. Minimum creep rate of Nickel 270 at 800°C

Y-48 348

Figure 63. Photomicrograph of Nickel 270 in the as-received condition. Etchant: acetic, nitric, and hydrochloric acids. 100x.

Y-48350

Figure 64. Photomicrograph of Nickel 270 after a 1-hr anneal in vacuum at 800°C. Etchant: acetic, nitric, and hydrochloric acids. 100x.

Y-53369

Figure 65. Nickel 270 tested in a hydrogen environment at 800°C and 1000 pounds per square inch. Test 2440. Photograph taken at the fracture with the specimen in the as-polished condition. 100x.

Y-53370

Figure 66. Nickel 270 tested in a hydrogen environment at 800°C and 1000 pounds per square inch. Test 2440. Photograph taken 1 in. from fracture. Etchant: acetic, nitric, and hydrochloric acids. 100x.

Y-53368

Figure 67. Nickel 270 tested in an argon environment at 800°C and 1000 pounds per square inch. Test 2612. Photograph taken 1 in. from fracture. Etchant: acetic, nitric, and hydrochloric acids. 100x.

in argon at 1000 pounds per square inch and 800°C. The structure is quite similar to that shown in Figure 66, page 141, for a specimen tested in hydrogen under similar test conditions. Hence, the microstructure of this material does not show any differences which might account for the different behavior in argon and hydrogen environments.

Stress-Rupture Properties of High-Purity Copper

To determine the generality of the reduction in creep strength due to hydrogen, tests were run on high-purity copper to compare its creep behavior in argon and in hydrogen environments. The results of several of these tests at 800°C are given in Table XV. Figure 68 depicts graphically the reduction in rupture life brought about by hydrogen. The influence of hydrogen seems to become greater as the stress (or strain rate) is reduced. The reduction in strength is quite large. For example (reading from Figure 68), a specimen at 580 pounds per square inch would fail in 1000 hr if in an argon environment and in about 40 hr if in a hydrogen environment. For these conditions, the fractional decrease in rupture life due to hydrogen is 0.96. From Figure 69 it is apparent that the minimum creep rate is accelerated by the presence of hydrogen. The data in Table XV also show that the rupture ductility is significantly less in hydrogen than in argon. Hence, hydrogen reduces the rupture life and the fracture ductility and increases the minimum creep rate.

The last two specimens listed in Table XV were annealed for 162 hr in hydrogen at 800°C prior to testing. Although this anneal

TABLE XV

CREEP-RUPTURE PROPERTIES OF HIGH-PURITY COPPER AT 800°C

(Annealed 1 hr at 800°C in vacuum prior to testing)

Test No.	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)
2204	750	Argon	93.5	73.4	100	2.23×10^{-1}
2296	600	Argon	821.9	20.3	49.8	1.14×10^{-2}
2146	500	Argon	3065.7	39.1	88.9	2.80×10^{-3}
2582 ^a	300	Argon	3118.3	3.47	2.78	4.80×10^{-4}
2298	600	Hydrogen	47.4	10.9	30.3	6.86×10^{-2}
2258	500	Hydrogen	105.1	26.6	15.4	3.20×10^{-2}
2148	434	Hydrogen	141.1	10.9	37.5	2.41×10^{-2}
2663	400	Hydrogen	641.3	12.5	19.9	7.17×10^{-3}
2471	300	Hydrogen	1617.9	7.81	4.30	1.68×10^{-3}
2205 ^b	500	Argon	668.5	23.4	57.9	1.33×10^{-2}
2287 ^b	500	Hydrogen	295.9	62.5	78.5	1.65×10^{-2}

^aTest discontinued prior to fracture of specimen.^bAnnealed 162.4 hr at 800°C in hydrogen.

Figure 68. Creep properties of high-purity copper at 800°C

Figure 69. Minimum creep rate of high-purity copper at 800°C.

seemed to reduce the magnitude of the influence of hydrogen, there still remains a significant influence of test environment.

Several of the specimens were analyzed after testing to determine whether significant changes in the interstitial impurity content had occurred during testing. These data are given in Table XVI. It is concluded from these results that the concentration of interstitial impurities did not change significantly during testing in argon or in hydrogen.

Several samples were examined metallographically to determine whether the microstructure was influenced by the test environment. Figure 70 is a photomicrograph of the copper after a 1-hr anneal at 800°C in vacuum. The fine "precipitates" are actually etch pits. Figure 71 illustrates the type of structure present in specimens tested in an argon environment. Many of the voids present seem to be associated with grain boundaries, whereas others do not. Figure 72 shows the structure of a specimen tested in a hydrogen environment. This specimen also contains numerous grain boundary voids. Figure 73 is a photograph of a specimen annealed for 162 hr in hydrogen at 800°C prior to testing in an argon environment at 800°C. Again, the most significant feature is the voids, many of which are present in the grain boundaries. The photographs presented indicate that the after-test microstructure does not seem to be influenced by whether the test environment is argon or hydrogen.

TABLE XVI

SUMMARY OF CHEMICAL DATA ON HIGH-PURITY COPPER IN WEIGHT PER CENT

	Hydrogen	Oxygen	Nitrogen	Carbon
As-received	< 0.0001	< 0.0005	< 0.0005	0.002
Test 2148 (141.1 hr at 800°C in H ₂)	< 0.0001	< 0.0005	< 0.0005	< 0.002
Test 2146 (3065.7 hr at 800°C in Ar)	< 0.0001	0.0010	< 0.0005	< 0.002
Test 2205 [Annealed 162.4 hr at 800°C in H ₂ , tested 668.5 hr at 800°C in Ar]	< 0.0001	0.0006	< 0.0005	
Test 2287 [Annealed 162.4 hr at 800°C in H ₂ , tested 296 hr at 800°C in H ₂]	< 0.0001	0.0009	< 0.0005	
Test 2471 [1617.9 hr at 800°C in H ₂]	< 0.0001	0.0005	< 0.0005	
Test 2298 [47.4 hr at 800°C in H ₂]	< 0.0001	< 0.0005	< 0.0005	
Test 2296 [821.9 hr at 800°C in Ar]	< 0.0001	< 0.0005	< 0.0005	
Test 2204 [93.5 hr at 800°C in Ar]	< 0.0001	0.0005	< 0.0005	

Y-51819

Figure 70. Photomicrograph of high-purity copper annealed 1 hr at 800°C in vacuum. Etchant: copper regia. 100X.

Y-51814

Figure 71. High-purity copper after testing at 600 pounds per square inch and 800°C in argon. Test 2296. Etchant: copper regia. 100X.

Y-51810

Figure 72. High-purity copper after testing at 300 pounds per square inch and 800°C in hydrogen. Test 2471. Etchant: copper regia. 100x.

Y-51806

Figure 73. High-purity copper after testing at 500 pounds per square inch and 800°C in argon. Annealed 162 hr at 800°C in hydrogen prior to testing. Test 2205. Etchant: copper regia. 100X.

Stress-Rupture Properties of Armco Iron - Heat R-121

Several tests were run in argon and in hydrogen environments to evaluate the creep and tensile properties of this material at 815°C. The results of these tests are summarized in Tables XVII and XVIII. The creep data are also represented in Figure 74 as a plot of the stress against the time to failure. The scatter in the experimental results is attributed to the nature of the test material rather than to the experimental techniques used. The reason for this will be discussed later. These data do not demonstrate any reproducible influence of hydrogen on the rupture life of this material. At a stress level of 500 pounds per square inch, the rupture life of a specimen tested in argon was 23 per cent less than a specimen tested in hydrogen (tests 1367 and 1361). At a stress level of 300 pounds per square inch, the opposite trend was observed with the rupture life in hydrogen 14 per cent less than that observed in argon (tests 1631 and 1571). In light of the scatter in the results, these differences are not considered significant. Figure 75 makes a comparison of the minimum creep rate and the applied stress. Again, considerable scatter was obtained, but no significant influences of hydrogen on the creep rate are evident.

The data in Table XVIII indicate that the fracture strains of this material are quite small for creep tests of 25 hr or greater duration. Because of the small magnitudes of the fracture strains and the extremely rough fracture surfaces, it was impossible to obtain accurate values of the total specimen elongation. The reduction-in-area measurement is believed to be a better ductility parameter for

TABLE XVII

SUMMARY OF TENSILE TESTS ON ARMCO IRON AT 815°C

Material Designation: R-121
Specimen Geometry: 0.375-in.-diameter rod
Condition of Material: As-received
Strain Rate: 2.0%/min

Environ- ment	Yield Strength (psi)	Ultimate Strength (psi)	Elongation (%)	Reduction in Area (%)
Argon	4100	4120	21.5	28.7
Hydrogen	4380	4380	20.5	28.7

TABLE XVIII

CREEP-RUPTURE PROPERTIES OF ARMCO IRON

Test Temperature: 815°C
 Specimen Geometry: 0.375-in.-diameter rod ×
 2.50-in.-gage section
 Condition of Material: As-received

Test No.	Stress (psi)	Environment	Rupture Life (hr)	Elongation of Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)
1324	3500	Hydrogen	0.15	22.5	28.16	--
1325	2500	Argon	1.5	17.5	19.72	1.19
1922	1500	Argon	23.2	3.75	2.65	3.80×10^{-2}
1340	1000	Argon	57.5	6.25	3.18	2.00×10^{-2}
1360	977	Hydrogen	57.9	5.00	3.71	1.36×10^{-2}
2045	650	Argon	313.8	3.75	2.12	4.90×10^{-3}
1367	500	Argon	368.1	8.75	3.44	5.25×10^{-3}
1361	500	Hydrogen	477.3	8.76	3.63	3.85×10^{-3}
1973	400	Argon	716.2	11.3	3.61	5.58×10^{-3}
1631	300	Argon	2285.5	8.76	3.63	1.745×10^{-3}
1571	300	Hydrogen	1956.1	13.0	5.80	1.69×10^{-3}
2124 ^{a,b}	300	Argon	837.5	1.25	1.33	1.25×10^{-3}
2122 ^a	300	Hydrogen	3114.6	26.3	17.1	2.54×10^{-3}

^aSpecimen annealed 208 hr at 1500°F in hydrogen prior to testing.

^bTest discontinued prior to failure of specimen.

Figure 74. Stress-rupture properties of Armco iron tested in argon and hydrogen at 815°C.

Figure 75. Creep properties of Armco iron tested in argon and hydrogen at 815°C.

this material. The reduction-in-area is plotted in Figure 76 as a function of the rupture life. For short rupture lives (or high strain rates), the ductility is reasonably high and decreases as the rupture life increases. There seems to be a tendency for the ductility to increase slightly for rupture lives in excess of 200 hr. Hydrogen does not seem to result in any measurable effects on the rupture ductility of this material.

Several of the test specimens were analyzed for carbon and sulfur after testing to determine whether significant quantities of these elements were lost due to exposure to hydrogen. The results of these analyses are given in Table XIX. It is difficult to rationalize the carbon content of the as-received material in light of the low concentrations found in the tested specimens. However, the important point is that the concentration of carbon and sulfur present in specimens tested in hydrogen was not significantly different from those found in specimens tested in argon. However, the hardness readings in Table XX indicate that hydrogen may have removed some impurity from the iron. This impurity was not necessarily carbon or sulfur, but may have been silicon or some other element.

A typical microstructure of the as-received material is shown in Figure 77. The stringers, which are characteristic of Armco iron, are normally quite high in silicon. Several very large stringers were located near specimen fractures and these are felt to be responsible for the scatter of the test results. Figures 78 and 79 are representative photomicrographs of the specimens from tests 1367 and 1361,

Figure 76. Ductility of Armco iron creep specimens tested at 815°C in argon and hydrogen.

TABLE XIX

SUMMARY OF CHEMISTRY RESULTS FOR ARMCO IRON (R-121)

Condition of Material	Carbon (wt %)	Sulfur (wt %)
As-received	0.040	0.020
	0.014	
Creep test 1631 (2285 hr in argon)	0.004	0.020
Creep test 1571 (1956 hr in hydrogen)	0.003	0.010
Creep test 1367 (368 hr in argon)	0.005	--
Creep test 1361 (477 hr in hydrogen)	0.002	--

TABLE XX

HARDNESS DATA ON ARMCO IRON (R-121)

Specimen Number	Average Hardness (DPH)
As-received	99.2
1367	73.3
1361	68.0
1631	61.6
1571	50.3

Y-41085

Figure 77. Photomicrograph of Armco iron (R-121) in the as-received condition. 100x.

Y-51435

Y-51434

Figure 78. Armco iron (R-121) stressed at 500 pounds per square inch in argon at 815°C. Ruptured after 368.1 hr with 8.75 per cent strain. Photomicrographs located 1 in. from fracture. 100X. Upper photograph made with specimen etched in 2 per cent nital; lower photograph made in as-polished condition.

Y-51437

Y-51436

Figure 79. Armco iron (R-121) stressed at 500 pounds per square inch in hydrogen at 815°C. Ruptured after 477.3 hr with 8.76 per cent strain. Photomicrographs located 1 in. from fracture. 100X. Upper photograph made with specimen etched in 2 per cent nital; lower photograph made in as-polished condition.

respectively. There is very little change in the grain structure of the material except for the profuse intergranular cracking which has occurred. Most of these cracks are oriented normal to the applied stress, and many appear to be made up of small voids joined together. No differences are apparent between the argon specimen illustrated in Figure 78, page 163, and the hydrogen specimen in Figure 79, page 164. Figures 80 and 81 compare the microstructures of specimens 1631 and 1571 tested in argon and hydrogen, respectively, at 300 pounds per square inch. These test conditions produced no change in the grain size of the material, but did result in the formation of grain boundary cracks. Again, many of these cracks were made up by the joining of small voids. There was a detectable influence of hydrogen on the stringers present in the specimen from test 1571. Many of the voids resulted from stringers from which material had been removed during the long exposure to hydrogen. However, this apparent chemical reaction did not significantly alter the creep properties of the material.

Stress-Rupture Properties of Electrolytic Iron

Several tests were run to determine whether the mechanical behavior of pure iron, in either the body-centered cubic or the face-centered cubic form, is altered by the presence of hydrogen. The results of these tests are summarized in Table XXI. Plots of stress versus rupture time and minimum creep rate are given in Figures 82 and 83, respectively. The test results on this material show a large amount of scatter, particularly at the 950°C test temperature.

Y-45592

Figure 80. Armco iron (R-121) stressed at 300 pounds per square inch in argon at 815°C. Ruptured after 2285.5 hr with 8.76 per cent strain. Photomicrograph located 0.75 in. from fracture. Etchant: 2 per cent nital. 100X.

Y-45589

Figure 81. Armco iron (R-121) stressed at 300 pounds per square inch in hydrogen at 815°C. Ruptured after 1956.1 hr with 13.0 per cent strain. Photomicrograph located 0.75 in. from fracture. Etchant: 2 per cent nital. 100X.

TABLE XXI

CREEP PROPERTIES OF ELECTROLYTIC IRON

(Material annealed 1 hr at 1000°C in hydrogen
prior to testing)

Test No.	Stress (psi)	Temp (°C)	Environ- ment	Rupture Life (hr)	Elongation at Rupture (%)	Reduction in Area (%)	Minimum Creep Rate (%/hr)
2767	1200	800	Argon	15.5	43.4	55.3	0.75
2665	1000	800	Argon	41.2	34.9	50.1	
2585	1000	800	Hydrogen	36.2	32.8	36.8	0.070
2668	650	800	Argon	196.6	21.1	27.1	0.019
2664	650	800	Hydrogen	229.7	23.4	35.5	0.0140
2343	500	800	Argon	701.0	22.7	29.4	0.0073
2454	500	800	Hydrogen	523.8	21.1	35.8	0.0058
2869	370	800	Argon	1754.1	20.3	29.4	0.0016
2915	390	800	Hydrogen	1129.5	14.8	52.5	0.0033
2868	1500	950	Argon	38.6	8.6	6.7	0.122
2720	1100	950	Argon	79.2	7.8	3.2	0.052
2974	950	950	Argon	230.2	8.6	7.1	0.018
2718	800	950	Argon	850.0	4.7	4.4	0.00267
2933	700	950	Argon	722.6	6.0	3.6	0.0036
2846	700	950	Argon	604.8	5.0	3.6	0.0047
2945	700	950	Hydrogen	639.0	8.2	5.1	0.0045
2801	600	950	Hydrogen	906.1	7.8	4.7	0.0037

Figure 82. Rupture life of electrolytic iron at 800 and 950°C.

Figure 83. Minimum creep rate of electrolytic iron at 800 and 950°C.

Although much of the scatter at 950°C can be attributed to difficulties associated with the measurement and control of temperature, the low ductility of the material is also a major factor. When a material begins to exhibit fracture strains as low as 5 per cent, it is quite sensitive to notches such as internal and surface flaws. The data at 800°C, where the iron is in the body-centered cubic form, do not show any significant influence of hydrogen with respect to rupture life, minimum creep rate, and rupture ductility. At 950°C where the iron is in the face-centered cubic form, the scatter in the experimental results makes a conclusion rather difficult. The clustering of data for argon and hydrogen environments at a stress level of 700 pounds per square inch indicates that the test environment is not an important factor. Hence, in light of the data presently available, it appears that the mechanical behavior of pure iron, both in the body-centered cubic and face-centered cubic forms, is not altered significantly by whether the test environment is argon or hydrogen.

The microstructure of the material after a 1-hr anneal at 1000°C in hydrogen is shown in Figure 84. Although the impurity content of this material is quite low, numerous inclusions are present. Examination at high magnification also reveals the presence of a substructure. The average grain diameter after annealing is about 0.012 cm. Figure 85 is a photomicrograph of a specimen tested at 800°C and 500 pounds per square inch in an argon environment. The structure is characterized by numerous grain boundary voids. These voids are preferentially oriented normal to the applied stress. Very little change in grain

Y-54656

Figure 84. Photomicrograph of electrolytic iron after annealing 1 hr at 1000°C in hydrogen. Etchant: 2 per cent nital. 100x.

Y-51433

Figure 85. Photomicrograph of electrolytic iron after testing at 800°C and 500 pounds per square inch in argon. Test 2343. Photograph taken 0.75 in. from fracture. Etchant: 2 per cent nital. 100x.

size occurred during the test. Figure 86 illustrates the structure of a specimen tested at 500 pounds per square inch and 800°C in a hydrogen environment. Again, the grain boundary voids are the predominant feature. Although some of the voids do not appear to be associated with grain boundaries, this is because the specimen did not etch evenly and some boundaries were not revealed. Similar features were noted in the specimens tested at 950°C. Some grain boundary voids were smaller and more numerous than observed at 800°C, but did not appear different in specimens tested in argon and hydrogen environments. Hence, there is no apparent influence of environment on the microstructure of the electrolytic iron.

Stress-Rupture Properties of Type 304 Stainless Steel

Several tests were run to determine whether the creep properties of type 304 stainless steel were different in argon and in hydrogen environments. The results of these tests are given in Table XXII. These results, as well as extensive metallographic studies, indicate that, under the conditions investigated, the properties of this material are not altered by whether the test environment is argon or hydrogen.

II. CREEP TESTS INVOLVING ALTERNATING ARGON AND HYDROGEN ENVIRONMENTS

Because of the metallurgical differences in specimens of the same material, the difficulty in reproducing test conditions, and the small variations in creep behavior being studied, tests were run in

Y-51431

Figure 86. Photomicrograph of electrolytic iron after testing at 800°C and 500 pounds per square inch in hydrogen. Test 2454. Photograph taken 0.75 in. from fracture. Etchant: 2 per cent nital. 100x.

TABLE XXII

SUMMARY OF CREEP DATA ON TYPE 304 STAINLESS STEEL

Material Designation: R-1103
Condition of Material: Annealed 1 hr at 1038°C
Specimen Geometry: 0.020-in. sheet
Test Temperature: 815°C

Test No.	Stress (psi)	Environment	Rupture Life (hr)	Elongation at Rupture (%)	Minimum Creep Rate (%/hr)
2799	7000	Argon	53.4	18.8	0.290
3151	7000	Hydrogen	51.8	18.4	0.300
3090	5800	Argon	182.3	22.0	0.080
3087	5800	Hydrogen	145.2	16.1	0.087
2825	5000	Argon	375.2	10.9	0.021
3089	5000	Hydrogen	356.2	12.2	0.024
2934	4000	Argon	1071.3	10.9	0.0058
3088	4000	Hydrogen	1095.0	9.8	0.0061
3150	3500	Argon	2002.4	10.6	0.0025
3152	3500	Hydrogen	1985.1	9.9	0.0023

which the test environment of a single specimen was alternated between argon and hydrogen. Although this procedure minimized the number and magnitude of the experimental variables, several difficulties still persisted. Due to the different properties of argon and hydrogen, the temperature distribution was changed by displacing one of these gases with the other. This change resulted in a change in the length of the pull rod system and hence a discontinuity in the strain measurements. It was also found that the strain rate had to be lower than 10^{-5} in./in.-hr to see an influence of environment. A further observation was that approximately 50 hr were required for the creep rate to change from that characteristic of one environment to that associated with another. Hence, it was necessary that the individual cycles be 100 to 200 hr in length to observe measurable strain under representative conditions. For example, in 200 hr at a strain rate of 1×10^{-5} , a 2-in. specimen would elongate 0.004 in. A change in room temperature of 3°C is enough to bring about the same apparent strain due to differential thermal expansion of the apparatus. Hence, there is considerable scatter in the test results and some cycles could not be analyzed.

The results of tests on electron-beam zone-refined nickel single crystals are summarized in Tables XXIII, XXIV, and XXV. The test described in Table XXIII was run at a fairly high strain rate, but shows a definite increase of the creep rate in hydrogen. Several cycles of this test are plotted in Figure 87. The important feature illustrated by this figure is that the creep rate goes through a transition period every time the environment is changed. The initial discontinuity

TABLE XXIII

COMPARISON OF THE CREEP RATES OF NICKEL (ELECTRON-BEAM
ZONE-REFINED) SINGLE CRYSTAL IN ARGON AND
HYDROGEN ENVIRONMENTS, TEST 1992

Stress: 2183 psi
Temperature: 815°C

Cycle No.	Environment	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate (in./in.-hr $\times 10^5$)
1 ^a	Hydrogen	300	300	---
2	Hydrogen	150	450	5.4
3	Argon	145	595	5.6
4	Hydrogen	190	785	5.6 to 80.6
5	Argon	175	960	80.6 to 25.3
6	Hydrogen	130	1090	35.1 ^b

^aVarious changes made in stress during this period.

^bTest discontinued.

TABLE XXIV

COMPARISON OF THE CREEP RATES OF NICKEL (ELECTRON-BEAM
ZONE-REFINED) SINGLE CRYSTAL IN ARGON AND
HYDROGEN ENVIRONMENTS, TEST 1688

Temperature: 927°C
Stress: 888 psi

Cycle No.	Environment	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate (in./in.-hr $\times 10^4$)
1 ^a	Argon	43.0	1219.4	0.88
2	Hydrogen	121.6	1341.0	1.56
3	Argon	75.3	1416.2	0.212
4	Hydrogen	90.9	1507.1	1.40
5	Argon	126.2	1633.1	0.695
6	Hydrogen	119.8	1751.9	1.48
7	Argon	97.6	1848.2	0.620
8	Hydrogen	168.1	2015.3	1.43
9	Argon	167.1	2182.4	0.720
10	Hydrogen	172.0	2353.4	1.364
11	Argon	118.4	2471.8	0.785

^aFirst 1176.4 hr of test were spent in short cycles at 815°C and 704°C. Cycles were too short to obtain useful information.

TABLE XXV

COMPARISON OF THE CREEP RATES OF NICKEL (ELECTRON-BEAM ZONE-REFINED)
IN HYDROGEN AND ARGON ENVIRONMENTS, TEST 2209

(Material annealed 1 hr at 1200°C in vacuum)

Specimen Geometry: 0.250-in.-diameter single crystal

Cycle No.	Environment	Temp (°C)	Stress (psi)	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate $\left(\frac{\text{in.}}{\text{in.-hr} \times 10^5}\right)$
1	Ar	814	1500-1910	310	310	a
2	Ar	814	1910	210	520	7.88
3	H ₂	813	1910	241	761	7.79
4	Ar	812	1910	177	938	6.00
5	H ₂	813	1910	162	1100	4.74
6	Ar	812	1910	241	1341	1.43
7	H ₂	812	1970	309	1650	6.42
8	Ar	815	1970	340	1990	2.93
9	H ₂	815	1970	315	2305	5.97
10	Ar	815	1970	400	2705	2.01
11	H ₂	815	1970	223	2928	6.60
12	Ar	813	1970	262	3190	2.15
13	H ₂	813	1970	162	3352	5.35
14	Ar	812	1970	168	3520	1.74
15	H ₂	813	1970	169	3689	5.02
16	Ar	812	1970	251	3940	2.17
17	H ₂	813	1970	160	4100	4.40
18	Ar	812	1970	268	4368	2.41
19	H ₂	815	1970	162	4530	4.68
20	H ₂	798	1970	340	4870	1.70
21	Ar	799	1970	170	5040	3.93
22	Ar	809	1970	237	5277	0.98
23	Ar	700	2270	173	5450	~ 0
24	H ₂	700	2270	263	5713	~ 0
25	Ar	701	2270	65	5778	~ 0
26	Ar	701	2575	102	5880	3.41
27	H ₂	702	2575	240	6120	2.95
28	Ar	701	2575	170	6290	1.89
29	H ₂	702	2575	190	6480	2.51
30	Ar	702	2575	170	6650	0.900
31	H ₂	701	2575	170	6820	2.24
32	Ar	701	2575	80	6900	0.887
33	H ₂	701	2575	250	7150	2.07

TABLE XXV (continued)

Cycle No.	Environ-ment	Temp (°C)	Stress (psi)	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate ($\frac{\text{in.}}{\text{in.-hr} \times 10^5}$)
34	Ar	701	2575	170	7320	----
35	H ₂	701	2575	170	7490	----
36	Ar	701	2575	160	7650	0.243
37	H ₂	701	2575	200	7850	1.81
38	Ar	701	2575	310	8160	0.68
39	H ₂	701	2575	170	8330	1.05

^aThis cycle used to adjust stress to give a reasonable strain rate.

Figure 87. Creep of nickel single crystal in argon and hydrogen environments at 815°C and 2183 pounds per square inch. Test 1992.

observed at the beginning of each cycle is due to the change in the temperature distribution in the apparatus, but the total transition period is some 50 hr long.

The test described in Table XXIV, page 179, illustrates a definite influence of hydrogen on this material at 927°C. Table XXV, pages 180 and 181 gives similar test results on a specimen at 815 and 700°C. The first four cycles show a continuously decelerating creep rate, but beginning with cycle 5 the creep rate alternates with the environment. Similar behavior was noted at 700°C. An effort was made to determine at which of the three investigated temperatures the influence of hydrogen was the greatest. Using the data in Table XXIV, page 179, for 927°C, the average creep rate in hydrogen is 2.22 times the creep rate in argon. The data in Table XXV, pages 180 and 181, for cycles 5 through 19 indicate that at 815°C the average creep rate in hydrogen is 2.55 times that in argon. Using cycles 28 through 39 in Table XXV, pages 180 and 181, a factor of two and ten hundredths was obtained for 700°C. Due to the scatter involved, it is difficult to attach any significance to the differences in these numbers and one must conclude that hydrogen exerts a similar influence over the temperature range of 700 to 927°C.

Data are presented in Tables XXVI through XXIX for Nickel 200 (R-1031). The test results summarized in Tables XXVI and XXVII were obtained at test temperatures of 800 and 815°C, respectively. The small number of cycles used for the tests make it difficult to draw any conclusions from the results, but no influences of test environment

TABLE XXVI

COMPARISON OF THE CREEP RATES OF NICKEL (R-1031) IN ARGON
AND HYDROGEN ENVIRONMENTS, TEST 1979

Stress: 1500 psi, annealed 1 hr at 815°C
prior to testing

Temperature: 800°C

Cycle No.	Environ- ment	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate (in./in.-hr $\times 10^4$)
1	Argon	160	160	1.19
2	Hydrogen	180	340	1.05
3	Argon	150	490	0.86
4	Hydrogen	180	670	0.84
5	Argon	170	840	1.21
6	Hydrogen	130	970	1.24
7	Argon	210	1180	1.27
8	Hydrogen	140	1320	1.47

Discontinued at 1320 hr with 15.95 per cent strain

TABLE XXVII

COMPARISON OF THE CREEP RATES OF NICKEL (R-1031) IN ARGON
AND HYDROGEN ENVIRONMENTS, TEST 1934, ANNEALED 1 HR AT
815°C PRIOR TO TESTING

Stress: 1500 psi

Temperature: 815°C

Cycle No.	Environ-ment	Duration of Cycle (hr)	Total Time		Strain Rate (in./in.-hr $\times 10^4$)
			at End of Cycle (hr)		
1	Hydrogen	163	163		2.94
2	Argon	172	335		1.05
3	Hydrogen	166	501		1.32
4	Argon	169	671		1.13
5	Hydrogen	164	834		2.31
6	Argon	148	982		3.17
Ruptured at 982.1 hr with 28.75 per cent strain					

TABLE XXVIII

COMPARISON OF THE CREEP RATES OF NICKEL 200 (R-1031) IN HYDROGEN
AND ARGON ENVIRONMENTS, TEST 1980

(Material annealed 1 hr at 815°C in vacuum prior to testing)

Specimen Geometry: 0.375-in.-diameter rod

Temperature: 704°C

Stress: 3500 psi

Cycle No.	Environ- ment	Duration of Cycle (hr)	Total Time		Strain Rate (in./in.-hr $\times 10^5$)
			at End of Cycle (hr)		
1	Ar	170	170		8.0
2	H ₂	160	330		8.8
3	Ar	180	510		6.0
4	H ₂	160	670		7.1
5	Ar	170	840		5.0
6	H ₂	150	990		5.6
7	Ar	170	1160		4.6
8	H ₂	190	1350		7.5
9	Ar	150	1500		5.8
10	H ₂	180	1680		9.6
11	Ar	170	1850		13.4
12	H ₂	160	2010		21.0
13	Ar	170	2180		11.0
14	H ₂	170	2350		16.0
15	Ar	50	2400		----

Test discontinued with 25.6 per cent strain.

TABLE XXIX

COMPARISON OF THE CREEP RATES OF NICKEL 200 (R-1031) IN HYDROGEN
AND ARGON ENVIRONMENTS, TEST 2247

(Material annealed 1 hr at 815°C in vacuum and
strained 5 per cent at room temperature)

Specimen Geometry: 0.375-in.-diameter rod

Temperature: 815°C

Stress: 1000 psi

Cycle No.	Environ- ment	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate (in./in.-hr $\times 10^4$)
1	Ar	170	170	2.65
2	H ₂	165	335	1.52
3	Ar	170	505	1.40
4	H ₂	165	670	1.07
5	Ar	170	840	0.974
6	H ₂	165	1005	0.940
7	Ar	170	1175	0.533
8	H ₂	165	1340	0.740
9	Ar	170	1510	0.754
10	H ₂	170	1680	0.880
11	Ar	165	1845	0.540
12	H ₂	165	2010	0.540
13	Ar	170	2180	0.540
14	H ₂	170	2450	0.707
15	Ar	170	2620	0.467
16	H ₂	235	2855	0.420
17	Ar	235	3090	0.615
18	H ₂	260	Rupture	1.25

are evident. The data given in Table XXVIII, page 186, for Nickel 200 (R-1031) were obtained at a test temperature of 704°C. These data illustrate conclusively a lower creep rate in argon than in hydrogen. The creep behavior of a specimen which was strained 5 per cent at room temperature prior to testing is illustrated by the data in Table XXIX, page 187. Under these test conditions, there is no difference in the creep rate in a hydrogen environment and that in an argon environment.

The creep of copper in argon and hydrogen environments is compared in Table XXX. This test was short, but the results show a definite indication that the creep rate is accelerated by hydrogen.

Table XXXI compares the creep rates of electrolytic iron in argon and hydrogen environments. There is no significant influence of environment under these conditions. This table also makes a comparison of the creep rates determined by a least squares technique and by visual estimation. The agreement is quite gratifying and the results obtained by visual estimation were utilized almost exclusively during the study.

III. RESULTS OF X-RAY EXPERIMENTS

Since efforts to reveal substructure by etching yielded inconsistent results, x-ray diffraction photographs were taken from heavily etched metallographic specimens using the back-reflection method. Unfiltered copper K_{α} radiation was used and the beam passed through a 25-mil collimator. The beam struck the center of the specimen about 0.75 in. from the fracture. Two-hour exposures were used.

TABLE XXX

COMPARISON OF THE CREEP RATES OF COPPER (99.999 Per Cent)
IN HYDROGEN AND ARGON ENVIRONMENTS, TEST 2757

(Material tested in as-received condition)

Specimen Geometry: 0.250-in.-diameter rod

Temperature: 600°C

Stress: 1000 psi

Cycle No.	Environ- ment	Duration of Cycle (hr)	Strain Rate (in./in.-hr $\times 10^5$)
1	Ar	165	5.74
2	H ₂	170	5.81
3	Ar	165	4.15
4	H ₂	170	5.84-7.58
5	Ar	118	7.00 → Rupture

TABLE XXXI

COMPARISON OF THE CREEP RATES OF IRON (ELECTROLYTIC)
IN HYDROGEN AND ARGON ENVIRONMENTS(Material annealed 1 hr at 1000°C
in hydrogen prior to testing)Specimen Geometry: 0.250-in.-diameter rod
Temperature: 800°C
Stress: 300 psi

Cycle No.	Environment	Duration of Cycle (hr)	Total Time at End of Cycle (hr)	Strain Rate ^a ($\frac{\text{in.}}{\text{in.-hr} \times 10^5}$)	Strain Rate ^b ($\frac{\text{in.}}{\text{in.-hr} \times 10^5}$)
1	Ar	167	167	1.61	1.56
2	H ₂	168	335	1.11	1.11
3	Ar	240	575	1.06	1.11
4	H ₂	167	742	1.07	1.17
5	Ar	268	1010	0.446	0.440
6	H ₂	170	1180	1.11	0.948
7	Ar	240	1420	0.694	0.723
8	H ₂	170	1590	0.650	0.932
9	Ar	190	1780	0.526	0.572
10	H ₂	170	1950	1.23	1.07
11	Ar	150	2100	1.19	1.06
12	H ₂	180	2280	1.15	1.14
13	Ar	170	2450	1.23	1.22
14	H ₂	190	2640	1.17	1.27
15	Ar	140	2780	1.04	1.09
16	H ₂	170	2950	1.69	1.67
17	Ar	195	3145	1.87	1.75
18	H ₂	310	3455	2.73	2.55
19	Ar	170	3625	2.39	2.41

^aDetermined by visual estimation.^bDetermined by least squares fit.

Several Nickel 200 (R-1031) and Inconel (NX892) specimens were examined by this technique. It was found that numerous grain sizes resulted from the various stresses and temperatures to which the creep specimens had been exposed. Although the grain size was markedly influenced by stress and temperature, there was no evidence that test environment significantly influenced the grain size or substructure formation.

IV. PERMEABILITY EXPERIMENTS

Large internal stresses due to hydrogen have been demonstrated at room temperature for steels which have been charged either by cathodic reduction of hydrogen ions on the surface or by rapidly cooling from higher temperatures where the hydrogen solubility is greater. However, the rapid diffusion rate of hydrogen in iron- and nickel-base materials at elevated temperatures makes it seem rather improbable that high internal pressures could be developed in these materials at elevated temperatures. To investigate the possibility that sufficiently high internal pressures could develop to affect creep, the experimental setup shown in Figure 6, page 39, was used for measurements on Inconel.

The conventional test arrangement for making permeability measurements involves the establishment of a constant pressure differential across a membrane of the material under study. The gas which permeates the membrane is collected and its volume measured. The rate of permeation of diatomic gases is usually found to be proportional to the difference of the square root of the pressures on the two sides of

the membrane (71). However, in the present experiments, the pressure differential was not maintained constant and the data were not amenable to conventional analysis. The curves shown in Figure 88 represent the data which were obtained. With the inner circuit initially evacuated and hydrogen flowing through the outer circuit, the hydrogen permeated into the inner circuit. If the outer circuit were purged with argon, the hydrogen in the inside circuit was evacuated. Gas samples were taken after both types of cycles to determine whether any appreciable concentration of hydrocarbons was present. Mass spectrometer analyses showed that the hydrocarbon concentration did not exceed 100 parts per million and was not significantly different at any point in the test. Observations were made over the temperature range of 700 to 927°C. It was concluded that the buildup of internal pressure in Inconel at elevated temperatures due to the presence of hydrogen was highly unlikely.

V. SURFACE ENERGY MEASUREMENTS IN ARGON AND HYDROGEN ENVIRONMENTS

No meaningful test results were obtained in this study, and the only purpose in including this topic is to raise some questions concerning the basic soundness of the zero creep techniques for determining the surface energy of metals. A virtual work argument is used to relate the balancing weight p and the surface free energy. For a small-diameter wire, three forces combine to balance the force applied to the wire. These forces include:

Figure 88. Permeation of hydrogen through Inconel at 815°C.

1. A longitudinal force created by the surface free energy.
2. A transverse compressive force due to the surface free energy.
3. A force due to the grain boundary free energy.

These terms combine to give the equation:

$$p = \lambda_s \pi r - \lambda_B n \pi r^2 \quad (8)$$

where p is the applied force, λ_s is the surface free energy, r is the radius of the wire, λ_B is the grain boundary free energy, and n is the number of grains per unit length. The last term causes only a 10 per cent error in λ_s and is often neglected. Hence, the surface free energy is given approximately by the load required to give a zero creep rate divided by πr (that is, $\lambda_s = p/\pi r$). The determination of p involves measuring the creep rate of small wires at several loads. Since the creep rate is measured by a macroscopic technique but is actually a microscopic process, the validity of this technique depends upon the specimen changing dimensions uniformly. The procedure normally used is that of putting different weights on several wires and annealing them at an elevated temperature. The specimens are removed periodically and measured to give a creep curve for each specimen consisting of about four points. In the present study, the creep rate of the specimen was measured continuously with time and it was found that the rate of contraction of the specimen decreased with time. The positive creep rates were linear when they were very small, but increased with time when the creep rate was moderately high. Hence, the creep rate varies

with time at a given stress and it is not possible to analyze the data. It is felt that the difficulty lies in the fact that each grain tends to minimize its surface area with the result that simple elongation or uniform contraction of the wire does not occur. The tendency is for the wire to become a series of spherical grains joined at single points. Hence, at constant load the stress changes considerably. The picture is further complicated by the fact that the specimen can elongate by dislocation motion on a certain type of plane or by low energy shear along a grain boundary if it is not normal to the applied stress. The net result is that the wire does not uniformly elongate (or contract) in one direction but rather elongates or contracts at certain points along the wire.

These complications are pointed out because of the extreme importance of establishing absolute values for the surface free energy of metals for use in analytical expressions describing the fracture of metals. Although these expressions are presently valuable to show the influence of variables such as temperature and grain size, their quantitative value would be enhanced if accurate values of the surface free energy were available. The basic techniques used to make such measurements deserve a very close examination.

VI. SINTERING OF NICKEL POWDERS IN DIFFERENT ENVIRONMENTS

Several tests have been run to compare the sintering rates of nickel powders in argon, vacuum, and hydrogen environments. The powders were hydrostatically pressed and surface machined into rods 0.25-in.

diameter $\times$ 2 in. long. Except for one set, the specimens were run in a quartz dilatometer so that the rate of densification could be measured. The results are somewhat contradictory in that some show a lower sintering rate in hydrogen than in argon or vacuum and other tests show no difference in these environments. The sintering rates in argon and vacuum were consistently the same. The results of one test which showed no difference are given in Table XXXII. The initial anneal in hydrogen was used to remove oxygen from the compact so that oxide particles would not be influential in the sintering. The interstitial content of the material after this anneal was found to be 70 parts per million carbon, less than 5 parts per million nitrogen, 76 parts per million oxygen, and 2 parts per million hydrogen. The data in Table XXXIII do not show any significant influence of hydrogen although the sintering rate is changing continuously with time. Figure 89 shows more clearly that the variations observed in the sintering rate are a function of time and not of environment.

The data in Table XXXIII for test E represent the other type of behavior. These data are also presented graphically in Figure 90 and show that the material sintered more rapidly in vacuum than in hydrogen.

The results of three additional tests in which the environment was not cycled are summarized in Table XXXIV. According to the dilatometer measurements, it appeared that the specimen in hydrogen underwent the least densification with those in argon and vacuum showing a smaller change. The densities measured after testing indicated that the specimen in hydrogen had the highest density. It is possible that

TABLE XXXII

SINTERING OF NICKEL POWDER AT 927°C, TEST F

(Specimen annealed 23 hr at 1000°C in
hydrogen and 1 hr at 1300°C in
vacuum prior to testing)

Cycle No.	Environ- ment	Sintering Rate $\left(\frac{\text{in.}}{\text{in.-hr} \times 10^{-5}} \right)$	Total Time at End of Cycle (hr)	Duration of Cycle (hr)	Midpoint ^a of Cycle (hr)
1	Vacuum	3.84	24	24	12
2	Argon	1.48	88	64	56
3	Hydrogen	1.28	135	47	112
4	Vacuum	0.94	183	48	159
5	Hydrogen	0.72	255	72	219
6	Vacuum	0.52	358	103	302
7	Hydrogen	0.37	451	93	405
8	Vacuum		524	73	561
9	Hydrogen	0.25	600	76	638

^aInformation used to plot curve in Figure 89.

Figure 89. Sintering of nickel powder at 927°C.

TABLE XXXIII

SINTERING OF NICKEL POWDER IN HYDROGEN AND VACUUM ENVIRONMENTS,
TEST E(Specimens annealed 1 hr at 1300°C in vacuum
prior to testing)

Cycle No.	Temp (°C)	Environ- ment	Sintering Rate ($\frac{\text{in.}}{\text{in.-hr}}$)	Total Time at End of Cycle (hr)	Duration of Cycle (hr)	Midpoint ^a of Cycle (hr)
1	927	Vacuum	5.92×10^{-5}	46	46	23
2	927	Hydrogen	2.52×10^{-5}	124	78	85
3	927	Vacuum	5.18×10^{-5}	166	42	145
4	927	Hydrogen	1.46×10^{-5}	189	23	178
5	927	Vacuum	3.8×10^{-5}	218	29	204
6	927	Hydrogen	0.99×10^{-5}	240	22	229
7	927	Vacuum	3.12×10^{-5}	308	68	274
8	927	Hydrogen	0.44×10^{-5}	363	55	336
9	927	Vacuum	2.06×10^{-5}	406	43	385
10	927	Hydrogen	0.23×10^{-5}	480	74	443
11	927	Vacuum	2.80×10^{-5}	520	40	500
12	815	Vacuum	~ 0	552	32	536
13	815	Hydrogen	~ 0	606	54	579
14	903	Hydrogen	~ 0	646	40	626
15	903	Vacuum	1.82×10^{-5}	670	24	658
16	982	Vacuum	4.04×10^{-5}	694	24	682
17	982	Hydrogen	1.3×10^{-5}	718	24	706

^aInformation used to plot curve in Figure 90.

Figure 90. Sintering of nickel powder.

TABLE XXXIV

SINTERING OF NICKEL POWDER IN DIFFERENT ATMOSPHERES AT 927°C

(All specimens annealed 24 hr at 1000°C in hydrogen
prior to testing)

Test Designation	Environment	Time at Temperature (hr)	Final Density (% Theoretical)
I	Vacuum	497.5	98.196
J	Hydrogen	495.1	98.379
K	Argon	486.7	98.205

this discrepancy can be accounted for by the specimens having different densities after the 24-hr anneal in hydrogen prior to the sintering anneal. The three specimens from tests I, J, and K were examined metallographically to determine whether there were significant differences in the number or size of voids. Representative photomicrographs are shown in Figures 91, 92, and 93. The number of voids per square inch was approximately 1×10^6 but was not significantly different for any of the three specimens.

One final attempt was made to resolve whether the sintering rate of nickel is different in argon and hydrogen. Six specimens from the same lot of material used in the rest of this study were annealed 24 hr at 1000°C in hydrogen and separated into two groups of three each. They were sintered 100 hr at 927°C — one group in argon and the other in hydrogen. The results of these tests are given in Table XXXV. There are large variations in the density after the 1000°C anneal in hydrogen. The changes in density as a result of the sintering anneals at 927°C are greater for the specimens which were less dense originally but do not reflect any influence of hydrogen. Hence, the large amount of scatter in the test results makes it impossible to draw a conclusion as to whether there is a difference in the sintering rate of nickel between argon and hydrogen environments.

Y-53092

Figure 91. Nickel powder annealed 24 hr at 1000°C in hydrogen and sintered 498 hr at 927°C in vacuum. Test I. 100x.

Y-53093

Figure 92. Nickel powder annealed 24 hr at 1000°C in hydrogen and sintered 495 hr at 927°C in hydrogen. Test J. 100X.

Y-53094

Figure 93. Nickel powder annealed 24 hr at 1000°C in hydrogen and sintered 487 hr at 927°C in argon. Test K. 100x.

TABLE XXXV

DENSITY OF NICKEL POWDER AFTER SINTERING 100 HR IN ARGON OR

HYDROGEN ENVIRONMENTS AT 927°C

(All specimens annealed 24 hr at 1000°C prior to testing)

Speci- men No.	Density after 24 hr at 1000°C (% Theoretical)	Environ- ment for Sintering Anneal	Density after 100 hr at 927°C (% Theoretical)	Change in Density due to Sintering (%)
1	97.218	Hydrogen	98.012	0.817
2	97.170	Hydrogen	97.830	0.679
3	95.518	Hydrogen	97.248	1.811
4	95.340	Argon	96.936	1.674
5	95.787	Argon	97.340	1.830
6	97.252	Argon	98.128	0.901

VII. COMPARISON OF THE SIZE AND GEOMETRY OF VOIDS FORMED DURING
THE INTERDIFFUSION OF IRON AND NICKEL IN ARGON AND HYDROGEN

Considerable time was spent in this program in finding suitable materials and a suitable procedure for making a diffusion couple. It was desired that the couple be made of nickel and a material of higher melting point so that the voids would be formed in the nickel. Molybdenum was first investigated as a material to form a couple with nickel. It was found that large voids were formed in the nickel, but the interface between the nickel and the molybdenum cracked on cooling due to the large difference in thermal expansion of the two materials. This made it difficult to examine the specimens metallographically.

Finally, diffusion couples of iron and nickel were prepared and run under the conditions summarized in Table XXXVI. The diffused couples were prepared for metallographic examination by etching in 2 per cent nital, which preferentially attacked the iron. Six or seven photomicrographs were taken across each specimen and these were joined together and rephotographed to obtain the composites shown in Figures 94, 95, and 96. There are several features worthy of note in the photographs. First, the bonding is not perfect. For example, the specimens in Figures 94 and 95 which were run in hydrogen show areas where contact was not made between the iron and the nickel. A second feature is that some voids were present in the iron (see Figures 95 and 96). These voids may have been sintered into the iron due to a microscopically rough surface on the iron specimen. This is supported by there

TABLE XXXVI

TEST CONDITIONS FOR IRON-NICKEL DIFFUSION COUPLES

Temperature (°C)	Time (hr)	Environment
927	751.0	Argon
927	751.0	Hydrogen
1091	398.2	Argon
1091	398.2	Hydrogen
1204	156.7	Argon
1204	156.7	Hydrogen

Y-46924

Fe - Ni DIFFUSION COUPLE
Annealed 751 Hrs. at 927 Degrees C in Argon

Fe - Ni DIFFUSION COUPLE
Annealed 751 Hrs. at 927 Degrees C in Hydrogen

Figure 94. Comparative iron-nickel diffusion couples at 927°C. Approximately 25X. Reduced 20 per cent

Y-46922

Fe - Ni DIFFUSION COUPLE

Annealed 398.2 Hrs. at 1091 Degrees C in Argon

Fe - Ni DIFFUSION COUPLE

Annealed 398.2 Hrs. at 1091 Degrees C in Hydrogen

Figure 95. Comparative iron-nickel diffusion couples at 1091°C. Approximately 25x. Reduced 20 per cent

Y-46923

Fe - Ni DIFFUSION COUPLE

Annealed 156.7 Hrs. at 1204 Degrees C in Hydrogen

Fe - Ni DIFFUSION COUPLE

Annealed 156.7 Hrs. at 1204 Degrees C in Argon

Figure 96. Comparative iron-nickel diffusion couples at 1204°C. Approximately 25x. Reduced 20 per cent

being fewer voids on the nickel side which indicates that less nickel diffused into the iron in these areas. The etching technique used left the nickel-rich areas unattacked. The light grain boundaries in Figure 94, page 209, illustrate the greater rate of diffusion along the grain boundaries at 927°C. At 1204°C (Figure 96, page 211) the advance of the nickel into the iron is uniform with grain boundaries offering no appreciable enhancement. The main feature to note in these specimens is that, if one gives due consideration to the inhomogeneous distribution of the voids and to apparent anomalies, there is no consistent difference between the specimens run in argon and those run in hydrogen. Attempts were made to determine the number of voids per unit length in each specimen and their total volume. These measurements were almost meaningless due to the difficulty of deciding whether some voids were a result of diffusion, a result of bad bonding, or other causes. Hence, it was felt that the overall visual examination technique was equally reliable. It was on this basis that it was concluded that the presence of hydrogen did not significantly influence the nucleation or growth of voids in nickel during the interdiffusion of nickel and iron.

VIII. INFLUENCE OF ARGON AND HYDROGEN ENVIRONMENTS ON THE RATE OF DIFFUSION OF COBALT-60 IN NICKEL

The results of diffusion experiments designed to determine whether hydrogen influences the rate of diffusion of cobalt-60 into nickel are shown in Figures 97 and 98. The slopes of log activity

Figure 97. Penetration plot of the diffusion of cobalt-60 into nickel after 446.2 hr at 1193°C.

UNCLASSIFIED
ORNL-LR-DWG 67233

Figure 98. Penetration plot of the diffusion of cobalt-60 into nickel after 1171 hr at 1095°C.

versus depth-squared plots are proportional to the diffusion coefficient since the paired specimens were machined to the same diameter. These results show that the rate of diffusion of cobalt-60 into nickel is not influenced by whether the specimen environment is argon or hydrogen. For the purpose of this work, it was not necessary to compute actual D values. However, values were computed for comparison with the results of other investigators. Good agreement was observed as shown in Table XXXVII. With an additional pair of diffusion couples, the annealing temperature varied from 1190 to 1166°C and the couple in argon was badly oxidized. The results of these diffusion couples indicated that the rate of diffusion was about 10 per cent greater with a hydrogen environment than with an argon environment. However, in light of the surface oxidation which occurred, these results are not deemed to be significant.

It is felt that the experimental accuracy realized with the four specimens is sufficient to warrant the conclusion that the rate of diffusion of cobalt-60 into nickel is not influenced by the environments, argon or hydrogen. Because of the similarity of the atomic sizes of cobalt and nickel, these results also imply that the rate of self-diffusion of nickel is not different in these environments. This in turn means that neither the concentration of vacancies nor their mobility is significantly different.

TABLE XXXVII
COMPARISON OF RESULTS WITH THOSE OF OTHER INVESTIGATORS

Temp (°C)	D (cm/sec ²)			ΔH (kcal/mole)		
	This Investigation	MacEwan ^a (calculated)	Hoffman ^b (calculated)	This Investigation	MacEwan ^a	Hoffman ^b
1193	1.71×10^{-10}	1.32×10^{-10}	1.40×10^{-10}	66.3	69.8	66.8
1095	3.42×10^{-11}	2.43×10^{-11}	2.71×10^{-11}			

^aJ. R. MacEwan et al., "Self-Diffusion in Polycrystalline Nickel," Can. J. Chem., 37, 1623 (1959).

^bR. E. Hoffman et al., "Self Diffusion in Solid Nickel," Trans. Met. Soc. AIME, 206, 483 (1956).

IX. CREEP STUDIES ON THIN NICKEL STRIPS

The material used in these studies was electron-beam melted (designated: electron-beam melted - ORNL) and rolled into thin sheet. The primary purpose in using thin specimens was to have specimens which subsequently could be thinned easily for electron transmission microscopy. Although the 0.060-in. $\times$ 0.0015-in. $\times$ 3-in. strip satisfied this requirement, it was rather unsatisfactory for mechanical property determinations. The sheared edges, the welded ends, and the large grain size all contributed to the large amount of scatter observed in the test results. However, certain information obtained from these studies is important and will be described briefly.

This material was first used in several tests to determine the activation energy for creep in argon and in hydrogen environments. The method involved making small temperature changes and measuring the resulting change in the steady-state creep rate. At the time these tests were run, it was not realized that several hours were required for the creep behavior to stabilize after the environment was changed. Hence, the environments were changed too frequently in the present tests and it is not surprising that different activation energies were not obtained. A representative set of data is shown in Figure 99. The numbers indicate the chronological order in which the readings were made. Points 1 through 6 were determined on material which had no pretest anneal. The activation energy obtained is 27,900 calories per mole. The specimen was then annealed in place for 1 hr at 1350°C. The

Figure 99. Creep of nickel strip in argon and hydrogen environments at elevated temperatures.

lower curve was then obtained from which an activation energy of 59,300 calories per mole is calculated. This value is in reasonable agreement with the 66,800 calories per mole obtained by Hoffman (72) for the activation energy for self-diffusion in nickel. The 27,900 calories per mole value obtained before the specimen was annealed is probably associated with grain boundary diffusion. Since the foils were quite thin, it was possible for deformation to occur almost solely by grain boundary movements which require a low activation energy. The 1350°C anneal resulted in the formation of a bamboo structure in which most of the grain boundaries were oriented normal to the specimen axis. The resolved grain boundary shear stress was quite small and deformation was controlled by bulk diffusional processes which require a higher activation energy.

The small fracture ductility of this material made it difficult to run creep tests in which the test environment was alternated between argon and hydrogen. One of the most successful tests is illustrated in Figure 100. This figure is inverted with respect to the normal creep curve since the chart record from the balance decreases as the specimen deforms. Although the creep rate continues to increase with test time, it is significant that the creep rate accelerates when the environment is changed to hydrogen and decelerates when changed to argon. This transition period covers approximately 50 hr.

Several of the tested specimens were examined by transmission electron microscopy. The relevant test data are summarized in Table XXXVIII and representative electron micrographs are given in

Figure 100. Creep of nickel strip in argon and hydrogen environments at 700°C.

TABLE XXXVIII

CREEP TESTS RUN USING NICKEL STRIP
(Electron-beam melted)

Test No.	Pretest Anneal	Test Temp (°C)	Stress (psi)	Environment	Rupture Life (hr)	Rupture Strain (%)
2164	None	825	2000	Argon	22.8	2.64
2163	None	825	2000	Hydrogen	11.8	4.59
2240	1 hr at 1300°C in argon	750	1000	Argon	328.4 ^a	0.40
2266	1 hr at 1300°C in argon	750	1000	Hydrogen	71.0 ^a	1.55

^aDiscontinued prior to failure.

Figures 101 through 104. Figure 101 illustrates the structure present after testing at low strain rates in argon. The dislocation density is $1.9 \times 10^9/\text{cm}^2$ and there are 3×10^{15} loops/ cm^3 . The dislocations will not move under the influence of the electron beam. Figure 102 illustrates the structure present after testing in hydrogen. The dislocation density in this specimen is $1.45 \times 10^8/\text{cm}^2$ and the dislocations move readily under the electron beam. The dislocation segments are reasonably straight with very little evidence of intersections. Figures 103 and 104 compare the structures obtained in specimens tested in argon and hydrogen environments at high strain rates. The structures are quite similar and are characterized by the presence of low angle boundaries (less than 1 degree) composed of walls of dislocations. It was again found that the dislocations moved readily in the specimen tested in hydrogen but would not move in the specimen tested in argon.

One further experiment using pieces of specimens from tests 2163 and 2266 indicated that the mobility of dislocations in specimens tested in hydrogen could be greatly decreased by removing the hydrogen. These pieces were annealed in vacuum 1 hr at 200°C to remove the hydrogen. After thinning, it was found that the dislocations would not move under the influence of the electron beam.

One further finding is illustrated by the photomicrographs in Figure 105. These not only illustrate the large grain size of the test specimens, but also show the lack of intergranular voids. Since large environmental influences were obtained without void formation, it seems that the influence of hydrogen on void growth cannot be the critical factor.

Figure 101. Transmission electron micrograph of nickel specimen from test 2240. 25,000X. Reduced 12 per cent.

YE-8888

Figure 102. Transmission electron micrograph of nickel specimen from test 2266. 25,000X. Reduced 9 per cent.

YE-8890

Figure 103. Transmission electron micrograph of nickel specimen from test 2164. 25,000X. Reduced 14 per cent.

Figure 104. Transmission electron micrograph of nickel specimen from test 2266. 40,000X. Reduced 12 per cent.

Figure 105. Photomicrographs of nickel strips tested at elevated temperatures. (a) Test 2164. (b) Test 2163. (c) Test 2240. (d) Test 2266. Etchant: acetic nitric, and hydrochloric acids. 100x. 3 per cent.

X. A COMPARISON OF THE RATES OF DIFFUSION OF CARBON IN NICKEL
IN ARGON AND IN HYDROGEN ENVIRONMENTS

Although six diffusion couples were run in this series, only one pair was sectioned. The data from this pair are presented in Figure 106. Additional samples were not sectioned because it was felt that the data from the first pair were conclusive. Although there were several sources of error, the annealing conditions provided sufficient diffusion penetration that the precision often required in diffusion measurements was not necessary in this case. The data in Figure 106 near the interface formed by the high and low carbon specimens are best represented by a single curve, indicating that the diffusion of carbon was not appreciably affected by whether the annealing environment was argon or hydrogen. There seems to be some difference in the carbon concentration gradient near the outer surfaces of the two specimens. This is probably related to the tendency of hydrogen to decarburize the material. However, some decarburization also occurred in the argon environment. This was probably due to the presence of trace quantities of oxygen in the argon which reacted with the carbon to form carbon dioxide. However, the slight differences in behavior at the surface are a result of different conditions existing at the specimen surface in the two environments and do not reflect a difference in the diffusion rate of carbon.

Figure 106. Effect of environment on the diffusion of carbon in nickel during a 300-hr anneal at 704°C.

CHAPTER V

DISCUSSION OF EXPERIMENTAL RESULTS

The purpose of this section is to tie together the results of the many experiments of this investigation and to show that each contributes to an understanding of how hydrogen influences the mechanical behavior of metals at elevated temperatures. The reasoning which preceded each experiment will be presented, the important results of each summarized, and the meaning of these results with respect to the present problem will be discussed.

This study was initiated because of the observation that the rupture life of Inconel was less in a hydrogen environment than in an argon environment at an equivalent stress and temperature. The first experiments undertaken were additional creep studies to better define the characteristics of the hydrogen influence. This involved looking at the effects of variables such as temperature, strain rate, cold working, grain size, carbon content, strain rate, and alloy composition.

The first series of tests which demonstrate the influence of several of these variables was run using Inconel (NX892) as a test material. These tests were run at 815°C with the material in the as-received condition. They showed:

1. That the influence of hydrogen became greater at lower strain rates.
2. That the rupture ductility is not appreciably influenced by hydrogen.

3. That the minimum creep rate is increased by hydrogen.
4. That the rupture life is in accord with that which would be predicted on the basis of the minimum creep rate.

Creep tests were run on another heat of Inconel (R-892) to determine how the influence of hydrogen varied with test temperature. These tests indicated qualitatively the same effects of hydrogen as those on the previous heat. The decrease in rupture life at 815°C due to hydrogen was only about 30 per cent for a 1000-hr rupture life for this heat as compared with a value of 67 per cent for the NX892 heat. The tests at 704°C using the R-892 material showed a decrease in rupture life due to hydrogen of only 12 per cent, thus indicating a greater influence of hydrogen at 815°C than at 704°C. Several specimens were annealed at temperatures up to 1204°C which gave a range of average grain diameters of 0.002 to 0.020 cm. Although these treatments changed the creep behavior of the material drastically, the fractional decrease in rupture life due to hydrogen was not changed significantly. A pair of specimens was also carburized to a carbon level of 0.124 per cent, and it was again found that this treatment changed the creep properties but not the influence of hydrogen.

Nickel 200 (R-1031) was tested at 593, 704, and 815°C. Again the influence of hydrogen was qualitatively the same as that observed for the NX892 heat of Inconel. The data indicate a reduction in the rupture life of the order of 40 per cent at 815°C, 25 per cent at 704°C, and 40 per cent at 593°C. The value at 593°C is based upon a relatively small amount of data so that probably the correct conclusion is that the

influence of hydrogen becomes greater at higher temperatures. The fractional reduction in rupture life due to hydrogen at 593°C was greater at the lower strain rates but did not exhibit a strain-rate dependence at 704 and 815°C. Annealing the material at elevated temperatures prior to testing slightly increased the influence of hydrogen. Annealing for an extended period in hydrogen failed to decrease the influence of hydrogen while the specimen was under stress. This indicates that hydrogen is not removing some impurity from the metal, but rather that hydrogen is influential in the deformation process. Prestraining 5 per cent at room temperature was found to inhibit the influence of hydrogen.

A very limited number of creep tests showed that the creep strength of electron-beam zone-refined nickel was also less in hydrogen than in argon. Both polycrystalline and single-crystal specimens were used.

Nickel 270 was found to also be adversely influenced by hydrogen. Again, the characteristics were similar to those observed for Inconel, but the magnitude is much greater than for any other material studied. The influence of hydrogen on this material did not exhibit any dependence on strain rate.

Because of the relatively high impurity level of the various lots of nickel, another high purity material with the face-centered cubic structure was sought. Copper was chosen and was found to be influenced by hydrogen much as was the Nickel 270, with the exception that the rupture ductility was less in hydrogen than in argon. Metallographic

studies and comparisons of the analyses of the test material before and after testing did not provide an explanation for decreased ductility in hydrogen. Because this material was quite low in oxygen and had inferior creep properties in hydrogen even after extended annealing in hydrogen, it was concluded that the reduction of copper oxide by hydrogen with the subsequent formation of water vapor did not contribute to the creep of this material.

Armco iron was tested to determine whether a body-centered cubic material behaved in hydrogen as did nickel and copper. No significant difference was noted between the properties of this material in argon and hydrogen environments. However, the large concentration of impurities made it a very undesirable test material and electrolytic iron was chosen for further tests. Tests were conducted at 800 and 950°C to provide the body-centered cubic and the face-centered cubic structures, respectively. It was found at both temperatures that the electrolytic iron was not influenced by hydrogen.

Type 304 stainless steel was also tested to determine its behavior in hydrogen. It was found to be similar to electrolytic iron in that it showed no influence of the hydrogen environment.

In summary, creep studies have shown that two heats of Inconel, Nickel 200, Nickel 270, electron-beam zone-refined nickel, and high-purity copper are influenced by a hydrogen environment. Several facts have been demonstrated. Hydrogen causes an increase in the secondary creep rate, a decrease in the time to rupture, and no significant change in the rupture ductility with the exception of copper. The fractional

decrease in the rupture life seems to become slightly greater with increasing test temperature. Several materials demonstrated increasing influence of hydrogen with decreasing strain rate. It was found that the minimum creep rate and the rupture life correlated well for tests in both argon and hydrogen environments. Several pretest annealing treatments were investigated which gave large variations in the creep behavior but did not cause very significant changes in the fractional decrease in the rupture life due to hydrogen. Small variations in the carbon content of Inconel did not significantly alter the influence of hydrogen. Long pretest anneals in hydrogen prior to creep testing did not reduce the influence of hydrogen. The only pretest treatment that did significantly alter the effects of hydrogen was prestraining. For Nickel 200, prestraining 5 per cent prior to creep testing greatly reduced the degradation of creep resistance by hydrogen. Tests on electron-beam zone-refined nickel demonstrated an influence of hydrogen on both single-crystal and polycrystalline materials.

Similarly, creep tests have shown that Armco iron, type 304 stainless steel, and electrolytic iron (body-centered cubic and face-centered cubic forms) have similar creep properties in argon and hydrogen environments.

In considering a mechanism to account for the observations just described, one of the first possibilities considered was whether this might be some variation of the slow strain-rate hydrogen embrittlement which is well known for low alloy steels. Cotterill (73) in summarizing the characteristics of this phenomenon sets forth at least two

characteristics which have not been observed in the present research. First, the ductility is reduced, and only one of the materials investigated in the present research showed any embrittlement due to hydrogen. Second, slow strain-rate embrittlement is effective over the temperature range of -100 to $+100^{\circ}\text{C}$, and the observations in this study were made over the temperature range of $+593$ to 927°C . Hence, the observations made in this study do not describe a slight variation of this phenomenon but rather a new high-temperature phenomenon due to hydrogen.

The next mechanism which was considered was that the properties were being altered due to the removal by hydrogen of some impurity from the metal which is essential to the creep strength of the material. This impurity might be carbon, oxygen, or sulfur. There are several factors which tend to discount this argument.

1. Numerous chemical analyses were made of creep specimens before and after testing, but it has been difficult to correlate analyses or changes in analyses with creep behavior because of several apparent anomalies. In general, the variations in analysis seem to be minor if not insignificant.
2. Metallographic examination revealed that the Inconel specimens had been decarburized to a depth of a few mils. However, creep tests on carburized specimens indicate that the strength of Inconel is not very sensitive to moderate changes in carbon content.

3. The fact that annealing for extended periods of time in hydrogen prior to applying a stress did not oblivate the influence of hydrogen during a creep test strongly discounts the removal of some impurity by hydrogen as an important factor.
4. The observation that the purer materials were influenced more by hydrogen also opposes the impurity mechanism.
5. The results of cyclic creep tests in which the test environment of a single specimen was alternated between argon and hydrogen are also important. These tests showed that those materials which were influenced by hydrogen exhibited one creep rate in hydrogen and a lower creep rate in argon. These creep rates were produced alternately as the test environment was cycled. This "reversibility" very definitely implies that this environmental effect is not due to the removal of an impurity by hydrogen.

The cyclic creep tests also demonstrated that the change from one creep rate to another did not occur immediately as the environment was changed but rather occurred over some 50 hr. This factor alone indicates that some rather complex process must be involved which does not depend on the diffusion of hydrogen into the material since hydrogen moves very rapidly through these materials at the temperatures of concern.

To determine whether there were significant differences in the recrystallization or polygonization tendencies of nickel during creep

tests in argon and hydrogen environments, a series of x-ray studies were made. Back-reflection patterns were made from polished cross sections of creep specimens of Inconel (NX892) and Nickel 200 (R-1031). These studies indicate that the substructure formed in both materials is primarily a function of the test temperature and the stress and is not significantly influenced by the test environment.

A large number of the creep specimens were examined metallographically after testing to determine whether there were significant differences in the microstructures of specimens tested in argon and those tested in hydrogen. No differences were observed. The specimens all exhibited intergranular fractures and contained numerous intergranular cracks. These cracks appeared in many cases to be composed of numerous voids, particularly in the Nickel 270 and the copper. Low strain rates and high temperatures favored the formation of intergranular voids.

One possible mechanism suggested early in this study was that the reduction of strength in hydrogen was due to the accumulation of gas in the grain boundary voids. This gas may come from the decomposition of carbides with the subsequent formation of methane or the reduction of oxides to form water vapor, but the resulting pressures would have to be higher than one atmosphere to significantly alter the creep behavior. Although the mobilities of the gaseous reactants and products at the temperatures of concern make the buildup of large pressures in internal voids seem unlikely, it is possible that the gas molecules may have difficulty dissociating and diffusing out of the

material. However, permeability experiments indicate that hydrogen and its reactions products are able to diffuse through Inconel readily and that a mechanism based on high pressures in internal voids is not reasonable.

The next step in reasoning was that the difference in creep properties might be associated with different growth rates of intergranular voids. A difference in the nucleation rate was discounted immediately since no difference was noted in the number of voids present in specimens tested in the two environments. Since the presence of voids is favored by high temperatures and low strain rates, a mechanism involving the rate of growth of voids would account for the influence of hydrogen being greater at high temperatures and low strain rates. Balluffi and Seigle (17) have worked out the thermodynamic conditions which favor the growth of voids in a metal under stress (see Equation 2, page 10). The surface energy of the voids is the driving force for the collapse of the voids which must be overcome by the applied stress if the voids are to grow. Hence, if the surface energy were lowered by the presence of hydrogen, the voids in a specimen in a hydrogen environment would be able to grow faster than those in a specimen in argon at the same stress level. Hence, several experiments were run to determine whether the surface energy was influenced by the presence of hydrogen.

Attempts to directly measure the surface energy of nickel in argon and in hydrogen environments did not produce reliable results. Hence, the rate of closed-pore sintering was investigated since this

rate should be an indirect measure of the surface energy. After a powder compact has sintered to the point where it consists of well-formed grains with closed pores, the surface energy of the voids is the driving force for further densification. Thus sintering occurs by the same driving force which must be overcome in the case of a creep experiment in order for voids to grow. Thus a reduction in surface energy should lead to higher rates of void growth under an applied stress and lower rates of densification (or void collapse) in a powder compact in the absence of applied stress. The sintering rates of nickel powders were compared in argon, vacuum, and hydrogen environments. The specimens were given a short sintering anneal, usually in hydrogen, before the rates were compared. Considerable scatter was observed in the test results and conclusions are difficult to make. The sintering rates were equivalent in argon and vacuum; in hydrogen, they were either equal to or less than those obtained in vacuum and argon environments.

It must be concluded that the attempts to determine whether the surface energy of nickel is different in argon and hydrogen are somewhat inconclusive. The sintering experiments give some indication that the surface energy may indeed be lower in hydrogen than in argon. Very little work has been reported in the literature with which to compare the present studies. Bailey and Watkins (74) found by use of thermal etching techniques that the ratio of the surface to the grain boundary energy of copper is equivalent in argon and hydrogen environments at 900°C. However, this does not necessarily mean that the surface and grain boundary energies are not both changed by the presence of

hydrogen. Several investigators have shown that different liquids appreciably alter the surface energy, but the reference quoted above is the only known reliable work comparing the surface energies of metals in different gases. Rhines et al. (75) concluded that the sintering rates of copper powder were equivalent in argon, hydrogen, and vacuum environments. Due to the scatter in their results, this conclusion may not be correct. Recent research by Brett and Seigle (76) compared the sintering rates of copper (dezincified brass) in argon and hydrogen environments at 1050°C. These studies showed that very little densification actually occurred, but metallographic examination revealed that some agglomeration of the voids did occur. The number of voids present in the specimen sintered in the argon environment was considerably less than the number present in the specimens sintered in hydrogen. This seems to indicate that the driving force for densification is greater in the argon environment and hence that the surface energy is greater. Hence, it seems that the present research and studies of other investigators give some indication that the surface energy of metals may be less in hydrogen than in argon, but the evidence is not conclusive.

The next reasoning advanced in this study was that the voids formed during creep might grow by somewhat more complex processes than those presently envisioned. Since Kirkendall diffusion results in the formation and growth of voids under a two-dimensional stress system caused by the unequal rates of material transport, a diffusion experiment seems to simulate the conditions in a creep test very nicely.

Nickel and iron were chosen for a diffusion couple since the nickel diffuses more rapidly with the result that voids should form in the nickel. Couples were run in argon and in hydrogen, but no effect of environment was observed on the size and distribution of voids in the nickel. Hence, neither the number nor the size of voids formed in creep and diffusion specimens is influenced by whether the environment is argon or hydrogen.

Another possible explanation for the influence of environment on creep would be an effect of hydrogen on the concentration or mobility of vacancies since these are involved in the mechanism of growth of void nuclei in creep specimens. Since the rate of self-diffusion is also controlled by these factors, studies of self-diffusion in pure nickel should indicate whether the number or mobility of vacancies is increased as a result of the presence of hydrogen in solution. A brief program was undertaken to study the diffusion of cobalt-60 into nickel in both argon and hydrogen atmospheres. This approach was taken because of the experimental ease of counting cobalt-60 as compared with nickel-63 and because the rate of diffusion of dilute quantities of cobalt-60 into nickel should illustrate the point equally well. These experiments showed that the rate of diffusion of cobalt-60 into nickel is not influenced by the presence of hydrogen.

The next important observation was made in examining the microstructure of a single-crystal specimen of the electron-beam zone-refined nickel which had exhibited significantly different creep properties in argon and hydrogen. It was noted that this specimen did not

contain any voids. Hence, the influence of environment on the growth rate of intergranular voids had to be eliminated as the important process.

The next experiments run involved thin nickel sheet creep specimens which could easily be further thinned for examination in the electron microscope. Tests in which the environment was alternated between argon and hydrogen showed that about 50 hr were required for the creep rate to stabilize after the environment was changed. This is in good agreement with the time required for large nickel specimens to change which is strongly indicative that the effect of hydrogen is an internal rather than a surface process. The electron transmission studies indicated that the dislocation density was higher in specimens tested in argon than in those tested in hydrogen. Numerous dislocation loops were also observed in the specimens tested in argon. The dislocations in the specimens tested in hydrogen moved readily under the thermal stresses introduced by the electron beam, whereas those in the specimens tested in argon did not move at all. If a specimen tested in hydrogen were annealed 1 hr at 200°C in vacuum to remove the hydrogen, the dislocations would not move as readily. These observations indicate that the dislocations are being pinned in the material tested in argon but not in the material tested in hydrogen. The observation that the dislocations are pinned by removal of the hydrogen indicates that the impurity atoms which are pinning the dislocations are not removed by the hydrogen but are redistributed. Hence, it seems that hydrogen in some way prevents the dislocations and the impurity atoms from interacting. There are at least two possible mechanisms that could account for this behavior. One

possibility is that the hydrogen atoms are preferentially clustered about the impurity atoms and inhibit their motion. Since the impurities were able to redistribute themselves during the 200°C anneal, the impurities of concern are probably interstitial, such as carbon. If such clustering does indeed occur and is effective in inhibiting the motion of the interstitial impurity, it would also reduce the bulk diffusion rate of the interstitial. On the premise that carbon is this impurity, a diffusion experiment was run to compare the diffusion rate of carbon in nickel in argon and hydrogen environments. This experiment showed that there was no influence of environment and hence tends to discount the clustering model. However, the possibility still remains that carbon is not the responsible impurity and that the clustering of hydrogen atoms around impurities is indeed the responsible mechanism.

Another mechanism that would prevent impurity-dislocation interactions is that the hydrogen is preferentially located along the dislocations and influences the strain fields of the dislocations so that the dislocation-impurity interactions do not occur or are not as effective. Several details of this model cannot be clearly postulated. The observation of Rogers (49) that the internal friction peak due to nitrogen increased when an iron wire was strained in a hydrogen atmosphere is of interest here. It was found that the dislocations did not release their nitrogen when the specimen was charged with hydrogen but only after the wire was strained. Hence, it seemed that the specimen had to be strained before the hydrogen became associated with the

dislocations. This factor would account for the observation that annealing alone does not change the creep properties but that the material must be under stress in hydrogen to see an influence of environment. The role of hydrogen would be to reduce the stress necessary for the formation of a dislocation loop of critical size. Thus, dislocations could be generated more easily in hydrogen, but they would also have to be able to move more easily. This may be tied in with the influence that hydrogen has on the strain field of a dislocation which allows it to move more easily. At high strain rates, the dislocation concentration becomes high and dislocation intersections are numerous. Under these conditions, dislocation intersection would provide the greatest obstacle to dislocation motion. At lower strain rates, the rate of dislocation annihilation would be comparable with the rate of generation and intersections would be less numerous and hydrogen would exert a greater influence. This would account for the observation that hydrogen exerts no influence at high strain rates. The fact that prestraining reduces the influence of hydrogen can also be accounted for in terms of the greater dislocation concentration in this material and the resulting more frequent dislocation intersections. Precipitates would also result in a more complex dislocation structure which would probably be influenced less by the presence of hydrogen. Thus, as observed experimentally, purer materials would be expected to show a greater influence of hydrogen. The long period of time required for the creep rate to change after the environment is changed in cyclic creep tests is necessary because of the time required for the

dislocations and impurity atoms to redistribute themselves. Thus, the proposed mechanism accounts qualitatively for all of the observations except the fact that iron-base alloys do not show an influence of hydrogen.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The experimental observation that the creep strength of Inconel was less in a hydrogen environment than in an argon environment stimulated a program to determine the characteristics of this hydrogen effect and the responsible mechanism. Creep experiments were run to compare the mechanical behavior of several metals in argon and hydrogen environments. The materials studied include two heats of Inconel, Nickel 200, Nickel 270, an electron-beam zone-refined melt of nickel, high-purity copper, Armco iron, electrolytic iron, and type 304 stainless steel. All of the nickel-base materials and copper exhibited inferior creep resistance in hydrogen, and the iron-base materials were not influenced by environment. Hydrogen had a large effect on pure nickel and copper with the magnitude decreasing with decreasing purity. The influence of hydrogen was generally found to exhibit the following characteristics:

1. At the same stress and temperature, the minimum creep rate is greater in a hydrogen environment than in argon.
2. The rupture life is less in hydrogen than in argon at an equivalent stress and temperature.
3. The rupture ductility is not influenced by hydrogen (copper excepted).
4. The rupture life and minimum creep rate are uniquely correlated independent of test environment.

5. If the test environment of a single specimen is alternated between argon and hydrogen, the creep rate will alternate also.
6. Some 50 hr are required for the creep rate to stabilize after the environment is changed. The same time is required for 0.375-in. diameter rods and 0.0015-in. thick foils.
7. Annealing at elevated temperatures prior to testing changes the creep characteristics but does not significantly alter the magnitude of the hydrogen effect.
8. The influence of hydrogen was not altered by small additions of carbon.
9. Prestraining seemed to reduce the influence of hydrogen.
10. Hydrogen exerted a larger influence with decreasing strain rate and increasing temperature.

Several possible mechanisms were postulated to account for these observations, and experiments were performed to check the validity of the postulations. It was concluded that the present phenomenon could not be accounted for in terms of the slow-strain rate hydrogen embrittlement which has been observed in steels since these two effects exhibit different characteristics. The possibility of chemical reactions between the test material and hydrogen was considered. However, chemical analyses failed to show conclusive evidence of the removal of significant quantities of any impurity from the test material. Characteristic No. 5 also tends to invalidate this possibility. The possibility of some reaction which might lead to the buildup of areas of

high pressure in the metal was also investigated. Permeability experiments discounted the mechanism by showing that hydrogen could move readily in and out of Inconel. X-ray examinations were made to determine whether specimens tested in the two environments exhibited any differences in structure. Within the accuracy of the method, no differences in substructure nor in residual working were evident. Metallographic examination failed to show any differences in specimens tested in the two environments. A significant feature noted in all specimens was intergranular voids which often joined together to form intergranular cracks. Several experiments were run to determine whether the influence of hydrogen was tied in with the growth rate of these voids. These studies showed that void growth is not influenced appreciably by whether the environment is argon or hydrogen. The importance of the voids was reduced by the observation that nickel single crystals showed influences of test environment but were found metallographically to contain no voids. Attention was then turned from mechanisms involving the void growth. Thin foil nickel specimens were creep tested in the two environments, thinned, and examined in the electron microscope. The observations indicated that dislocation pinning is more prevalent in an argon atmosphere and gave indication that hydrogen does not remove impurities from the metal but only results in the redistribution of the impurities present. These results suggest a mechanism in which the hydrogen atoms in solution in the metal form atmospheres around the impurity atoms and prevent them from interacting with the dislocations. On the premise that carbon is the impurity most

likely to produce the observed behavior, diffusion experiments were run with the results tending to invalidate a mechanism based upon atmospheres of hydrogen atoms forming around impurity atoms.

The mechanism thought to be most consistent with the experimental observations is based on the interaction of hydrogen with dislocations. The impurities present in the metal are normally associated with the dislocations. As new dislocations are generated, they become associated with the hydrogen atoms. There is some evidence that the stress required to produce a critical-size dislocation loop would be less under such circumstances. It is probable that the presence of the hydrogen atoms would alter the stress field of a dislocation so that its interaction with other impurity atoms or precipitates would not occur or would not be as effective. Conditions, such as high strain rates, prestraining, and large quantities of precipitates, would result in numerous dislocation intersections which probably would not be influenced by the presence of hydrogen. The large amount of time required for the creep rate to change after the environment is changed is necessary for the impurity atoms to be redistributed.

There is no known explanation for the fact that iron-base materials do not show an influence of hydrogen, whereas copper and nickel-base materials do. The only possible explanation is based on the fact that the solubility of hydrogen is less in iron than in the other two materials. This would in turn influence the quantity of hydrogen present in solution.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

REFERENCES

1. D. McLean, Mechanical Properties of Metals, Wiley, New York, 1962.
2. G. E. Dieter, Jr., Mechanical Metallurgy, McGraw-Hill, New York, 1961.
3. J. E. Dorn (ed.), Mechanical Behavior of Materials at Elevated Temperatures, McGraw-Hill, New York, 1961.
4. J. Frenkel, "Zur Theorie der Elastizitätsgrenze und der Festigkeit Kristallinischer Körper," Z. Physik, 37, 572 (1926).
5. J. K. Mackenzie, thesis, University of Bristol, 1949. (Unpublished, for details see A. Seeger, "Kristallplastizität," Encyclopedia of Physics, Vol. VII, p +2 (ed. by S. Flügge), Springer-Verlag, Berlin, Germany, 1958, p 1).
6. L. S. Darken, "Some Observations on Atoms and Imperfections," Am. Soc. Metals, Trans. Quart., 54, 599 (1961).
7. G. I. Taylor, "The Mechanism of Plastic Deformation of Crystals," Proc. Roy. Soc. (London), Ser. A, 145, 362 (1934).
8. E. Orowan, "Plasticity of Crystals," Z. Physik, 89, 605 (1934).
9. M. Polanyi, "Lattice Distortion which Originates Plastic Flow," Z. Physik, 89, 660 (1934).
10. E. W. Müller, "Field Emission Microscopy of Clean Surfaces with Electrons and Positive Ions," Ann. N.Y. Acad. Sci., 101, 585 (1963).
11. B. L. Averbach, D. K. Felbeck, G. T. Hahn, and D. A. Thomas (eds.), Fracture, Technology Press of MIT and Wiley, New York, 1959.
12. D. McLean, Mechanical Properties of Metals, pp 235-240, Wiley, New York, 1962.
13. C. Zener, Elasticity and Anelasticity of Metals, University of Chicago Press, Chicago, 1948.
14. R. D. Gifkins, "A Mechanism for the Formation of Intergranular Cracks when Boundary Sliding Occurs," Acta Met., 4, 98 (1956).
15. C. W. Chen and E. S. Machlin, "On a Mechanism of High Temperature Intercrystalline Cracking," Trans. Met. Soc. AIME, 209, 829 (1957).

16. E. S. Machlin, "Creep-Rupture by Vacancy Condensation," Trans. Met. Soc. AIME, 206, 106 (1956).
17. R. W. Balluffi and L. L. Seigle, "Growth of Voids in Metals During Diffusion and Creep," Acta Met., 5, 449 (1957).
18. J. N. Greenwood, D. R. Miller, and J. W. Suiter, "Intergranular Cavitation in Stressed Metals," Acta Met., 2, 250 (1954).
19. D. McLean, "A Note on the Metallography of Cracking During Creep," J. Inst. Metals, 85, 468 (1956-57).
20. G. Shinoda, T. Sano, and T. Sakurai, "Creep Rupture Strength and Changes in Microstructure of Austenitic Stainless Steels," J. Japan Inst. Metals (Sendai), 24, 818 (1960).
21. P. W. Davies and B. Wilshire, "The Effect of Grain Boundary Migration on Creep Ductility," Trans. Met. Soc. AIME, 221, 1265 (1961).
22. F. N. Rhines and P. J. Wray, "Investigation of the Intermediate Temperature Ductility Minimum in Metals," Trans. Am. Soc. Metals, 54, 117 (1961).
23. P. Cotterill, "The Hydrogen Embrittlement of Metals," Progress in Materials Science, 9(4), 205 (ed. by Bruce Chalmers), Pergamon Press, London, 1961.
24. D. P. Smith, Hydrogen in Metals, p XI, University of Chicago Press, Chicago, 1948.
25. C. E. Ransley, "Book Review: 'Hydrogen in Metals,' D. P. Smith," Met. Abstr. J. Inst. Metals, 16(858) (1949).
26. S. Dushman, Scientific Foundations of Vacuum Technique, Wiley, New York, 1960.
27. R. M. Barrer, "Aspects of Gas-Metal Equilibrium, Interstitial Solution and Diffusion," Discussions of the Faraday Society, 4, 68 (1948).
28. F. R. Bichowski and L. C. Copeland, "The Heat of Formation of Molecular Hydrogen," J. Am. Chem. Soc., 50, 1315 (1928).
29. L. Pauling, "Atomic Radii and Interatomic Distances in Metals," J. Am. Chem. Soc., 69, 542 (1947).
30. R. M. Brick and A. Phillips, Structure and Properties of Alloys, 2nd. ed., p 239, McGraw-Hill, New York, 1949.

31. H. W. Woolley, R. B. Scott, and F. G. Brickwedde, "Compilation of Thermal Properties of H in Its Various Modifications," J. Res. Nat. Bur. Std., A, 41, 379 (1948).
32. L. Luckemeyer-Hasse and H. Schenck, "Solubility of H in Fe, Cr, Ni, Mn, and Some Alloys," Arch. Eisenhüttenw., 6, 209 (1932).
33. G. Phragmén, "Relationship Between the Hydrogen Content of Iron, Temperature, and Equilibrium Hydrogen Pressure," Jernkontorets Ann., 128, 537 (1944).
34. A. Krupkowski and M. Smialowski, "Deformation in Iron Rods Under the Influence of Hydrogen Penetration," Arch. Hutnictwa, 1, 101 (1956).
35. A. Janko, "X-ray Studies of Nickel Charged Electrolytically with Hydrogen," Bull. Acad. Polon. Sci., Ser. Sci. Chim., 8, 131 (1960).
36. A. Wurtz, "Formation of a Cuprous Hydride, by the Action of Hypophosphorus Acid on a Cupric Salt Solution," Ann. Chim. Phys., 11, 250-252 (1844).
37. J. D. Fast, "The Permeability of Metal Walls for Gases," Phillips Tech. Rev., 6, 365 (1941).
38. I. Jenkins, "Some Developments in the Annealing of Malleable White Iron," Metal Treat. Drop Forging, 14, 175 (1947).
39. O. Z. Rylski, Diatomic Gases in Metals and Hydrogen Embrittlement of Titanium, PM 203, Department of Mines and Technical Surveys, Mines Branch, Ottawa, Canada, April, 1956.
40. D. N. Williams, "The Hydrogen Embrittlement of Titanium Alloys," J. Inst. Metals, 91, 147 (1962-63).
41. C. M. Schwartz and M. W. Mallett, "Observations on the Behavior of Hydrogen in Zirconium," Trans. Am. Soc. Metals, 46, 640 (1954).
42. L. L. Marsh et al., Effect of Hydrogen on the Tensile Transition in Uranium, USAEC Report BMI 980 (February, 1955).
43. H. E. McCoy and D. A. Douglas, Columbium Metallurgy (ed. by D. L. Douglass and F. W. Kunz), p 85, Interscience Publishers, New York, 1961.

44. B. W. Roberts and M. C. Rogers, "Observations on Mechanical Properties of Hydrogenated Vanadium," J. Metals, 8, 1213 (1956).
45. B. W. Roberts et al., "Hydrogen Embrittlement of Vanadium by Catalytic Decomposition of Water with Manganese," Trans. Met. Soc. AIME, 212, 71 (1958).
46. J. B. Seabrook et al., "Hydrogen Embrittlement of SAE 1020 Steel," Trans. Met. Soc. AIME, 188, 1317 (1950).
47. J. D. Hobson and C. Sykes, "Effect of Hydrogen on the Properties of Low-Alloy Steels," J. Iron Steel Inst. (London), 169, 209 (1951).
48. C. E. Sims and G. A. Moore, "The Effect of Hydrogen on the Ductility of Cast Steels," Trans. Met. Soc. AIME, 176, 283 (1948).
49. H. C. Rogers, "A Yield Point in Steel Due to Hydrogen," Acta Met., 2, 167 (1954).
50. A. Cracknell et al., "Hydrogen and the Yield Point in Steel," Acta Met., 3, 200 (1955).
51. C. L. M. Cottrell, "Delayed Brittle Fracture of Alloy Steel at Low Stress Levels," Nature (London), 170, 1079 (1952).
52. N. J. Petch and P. Stables, "Delayed Fracture of Metals Under Static Load," Nature (London), 169, 842 (1952).
53. W. J. Barnett and A. R. Troiano, "Crack Propagation in the Hydrogen-Induced Brittle Fracture of Steel," J. Metals, 9, 486 (1957).
54. W. A. Bell and A. H. Sully, "Some Effects of Hydrogen on the Delayed Fracture of High-Tensile Steel," J. Iron Steel Inst. (London), 178, 15 (1954).
55. C. A. Zapffe, "Research Shows How Pickling Causes Brittleness in Stainless Steels," Materials and Methods, 32, 58 (1950).
56. N. J. Petch, "The Lowering of Fracture-Stress Due to Surface Adsorption," Phil. Mag., 8(4), 331 (1956).
57. F. de Kazinczy, "A Theory of Hydrogen Embrittlement," J. Iron Steel Inst. (London), 177, 85 (1954).
58. H. G. Vaughan and M. E. de Morton, "An Effect of Hydrogen on the Hardness of Mild Steel," J. Iron Steel Inst. (London), 182, 389 (1956).

59. H. G. Vaughan and M. E. de Morton, "Hydrogen Embrittlement of Steel and Its Relation to Weld Metal Cracking," Brit. Welding J., 4, 40 (1957).
60. H. C. Rogers, "The Influence of Hydrogen on the Yield Point in Iron," Acta Met., 4, 114 (1956).
61. A. R. Troiano, "The Role of Hydrogen and Other Interstitials in the Mechanical Behavior of Metals," Trans. Am. Soc. Metals, 52, 54 (1960).
62. N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys, Dover Publications, New York, 1936.
63. P. Blanchard and A. R. Troiano, "La fragilisation des métaux par l'hydrogene, Influence de la structure cristallographique et électronique," Mem. Sci. Rev. Met., 57, 409 (1960).
64. T. E. Scott and A. R. Troiano, Interstitial Induced Delayed Failure of Steel, ARL 62-425, Aeronautical Research Laboratories, Office of Aerospace Research, U.S. Air Force, September, 1962.
65. S. Harper et al., "The Embrittlement of Tough-Pitch Copper Windings in Hydrogen-Cooled Electric Generators," J. Inst. Metals, 90, 414 (1961-62).
66. Ibid., p 423.
67. D. A. Douglas, High Temperature Materials, p 429 (ed. by R. F. Hehemann and G. M. Ault), Wiley, New York, 1959.
68. S. J. Klima et al., Preliminary Investigation of Effect of Hydrogen on Stress-Rupture and Fatigue Properties of an Iron-, a Nickel-, and a Cobalt-Base Alloy, Technical Note D-1458, Lewis Research Center, Cleveland, Ohio, 1962.
69. N. N. Kolgatin et al., "Rupture Strength of Tubular Steel Specimens under Internal Hydrogen Pressure at High Temperatures," Metalloved. i Term. Obrabotka Metal., 3, 19 (1959). [For English translation, see Metal Sci. Heat. Treat. Metals (USSR) Henry Bratcher Translation 4539].
70. D. McLean, Grain Boundaries in Metals, p 58, Oxford University Press, London, 1957.
71. W. Jost, Diffusion in Solids, Liquids, Gases, p 306, Academic Press, New York, 1960.

72. R. E. Hoffman et al., "Self-Diffusion in Solid Nickel," Trans. Met. Soc. AIME, 206, 483 (1956).
73. P. Cotterill, "The Hydrogen Embrittlement of Metals," Progr. Mater. Sci., 9, 231 (1961).
74. G. L. J. Bailey and H. C. Watkins, "Surface Tensions in the System Solid Copper-Molten Lead," Proc. Phys. Soc. (London), 63B, 350 (1950).
75. F. N. Rhines, C. E. Birchenall, and L. A. Hughes, "Behavior of Pores during the Sintering of Copper Compacts," Trans. Met. Soc. AIME, 188, 378 (1950).
76. J. Brett and L. Seigle, "Shrinkage of Voids in Copper," Acta Met., 11, 467 (1960).

APPENDIX

TEST MATERIALS

The pertinent chemical data along with the source and shape of the test materials are given as follows:

Material:	Nickel 200	Original Form:	1-in.-diameter rod
Designation:	R-1031	Source:	Unknown

Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Oxygen	0.0038
Nitrogen	0.0017
Carbon	0.037
Chromium	0.0005
Iron	0.1157
Sulfur	0.0008
Silicon	0.0345
Phosphorus	0.0115
Titanium	0.0110
Manganese	0.26
Cobalt	0.028

Several rods of material were used with the assumption that they were from the same heat. Later findings revealed that this was probably not the case. Several specimens were analyzed and it was found that their compositions were in the following ranges: (1) carbon, 0.023-0.054 weight per cent, (2) chromium, 0.0005-0.0033 weight per cent, (3) manganese, 0.22-0.23 weight per cent, (4) iron, 0.0492-0.1237 weight per cent, (5) silicon, 0.03 weight per cent, and (6) cobalt, 0.025-0.030 weight per cent. Four analyses on the same piece of material showed ranges of (1) carbon, 0.026-0.030 weight per cent, (2) iron, 0.0492-0.0538 weight per cent, and (3) cobalt, 0.026-0.030 weight per cent.

Material: Nickel 270
Designation: U. T.

Original Form: 0.75-in.-diameter
rod

Source: International Nickel
Company

Analysis

<u>Element</u>	<u>Content (weight per cent)</u>
Aluminum	0.001-0.01
Copper	0.0001-0.001
Magnesium	0.0001-0.001
Silicon	0.001-0.01
Carbon	0.0050
Hydrogen	0.0003
Oxygen	0.0130
Nitrogen	< 0.0005
Sulfur	0.0010
Phosphorus	0.0002

Material: Nickel 270
Designation: Heat 327

Original Form: 0.50-in.-diameter
rod

Source: International Nickel
Company

Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Aluminum	0.001-0.010
Cobalt	0.01-0.10
Copper	0.0001-0.0010
Iron	0.001-0.010
Silicon	0.001-0.010
Carbon	0.0060, 0.0070, 0.0020
Hydrogen	0.00034
Oxygen	0.0130
Nitrogen	< 0.0005
Sulfur	0.0010
Phosphorus	0.0003

Material: Nickel Original Form: Single crystals,
 Designation: Electron-beam 0.25-in. diameter
 zone-refined and various lengths
 Source: Materials Research Corporation, Yonkers, New York

Vendor's AnalysisORNL's Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>	<u>Content</u> <u>(weight per cent)</u>
Nitrogen	0.000002	< 0.0005
Oxygen	0.000093	0.0054
Hydrogen	0.000007	0.0003
Carbon	0.0040	
Aluminum	< 0.0030	0.001-0.010
Copper	< 0.0010	0.001-0.010
Iron	< 0.0016	0.01-0.10
Magnesium	< 0.0010	0.001-0.01
Manganese	< 0.0010	0.01-0.10
Silicon	< 0.0010	0.001-0.01
Chromium		0.0001-0.0010
Molybdenum		0.01-0.10

Material: Nickel Original Form: Material was melted
 Designation: Electron-beam into a thin disk
 melted about 0.25 in. thick
 and 3-in. diameter
 Source: Oak Ridge National Laboratory

Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Aluminum	0.001-0.010
Chromium	0.0001-0.0010
Copper	0.001-0.010
Iron	0.01-0.10
Manganese	0.01-0.10
Silicon	0.01-0.10
Titanium	0.001-0.010
Carbon	< 0.0010
Hydrogen	0.0002
Oxygen	0.0018
Nitrogen	< 0.0005
Sulfur	0.0030
Phosphorus	0.0007

Material: Nickel Original Form: 0.875-in. diameter rod
 Designation: Nivac P Source: Sanderson Holcomb Works, Syracuse, New York

Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Carbon	0.007
Manganese	< 0.002
Chromium	< 0.001
Aluminum	0.003, 0.006
Calcium	0.001, 0.01
Cobalt	0.09
Copper	0.003, 0.006
Iron	0.01, 0.05
Magnesium	< 0.001
Oxygen	0.0018

Material: Copper Original Form: 0.75-in.-diameter rod
 Designation: High purity
 Source: American Smelting and Refining Company Subsequent Fabrication: Material was cold swaged to 0.50-in. diameter

Vendor's Analysis: No metallic impurities detectable by spectrographic analysis

ORNL's Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Hydrogen	< 0.0001
Oxygen	< 0.0005
Nitrogen	< 0.0005
Carbon	0.002

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Carbon	0.042
Chromium	18.10
Nitrogen	9.76
Manganese	1.42
Phosphorus	0.023
Silicon	0.46
Sulfur	0.010

Material:	Iron	Original Form:	Block 2 in. x 2 in. x 24 in.
Designation:	Electrolytic	Source:	Unknown

ORNL's Analysis: ORNL spectrography analysis indicated that silicon present in the range of 10-100 parts per million was the only metallic impurity.

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Carbon	0.010, 0.0180
Oxygen	0.016
Nitrogen	0.0007

Material: Armco iron Original Form: 1-in.-diameter rod
 Designation: R-121 Source: Unknown

Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Oxygen	0.080, 0.081
Nitrogen	0.0020, 0.0025
Carbon	0.040, 0.014
Sulfur	0.020

Material: Inconel alloy 600 Original Form: 0.875-in.-diameter rod
 Designation: R-892 Source: Unknown

Analysis

<u>Element</u>	<u>Content</u> <u>(weight per cent)</u>
Oxygen	0.0036
Nitrogen	0.024
Carbon	0.05
Chromium	16.00
Iron	8.06
Sulfur	0.005
Silicon	0.26
Phosphorus	0.0085
Titanium	0.25
Manganese	0.25
Nickel	74.64

Material:	Inconel alloy 600	Original Form:	0.125-in. thick sheet
Designation:	NX892	Source:	Unknown

Analysis

<u>Element</u>	<u>Content (weight per cent)</u>
Oxygen	0.025
Nitrogen	0.014
Carbon	0.076 ^a
Chromium	15.84
Iron	9.36
Sulfur	0.0075 ^b
Silicon	0.20
Phosphorus	0.0095
Titanium	0.29
Manganese	0.31
Nickel	72.93

^aAverage of three determinations: 0.13, 0.06, 0.04.

^b Average of two determinations: 0.005, 0.10.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ORNL-3600

UC-25 - Metals, Ceramics, and Materials
TID-4500 (30th ed.)

INTERNAL DISTRIBUTION

1-3. Central Research Library	53-54. H. E. McCoy
4. Reactor Division Library	55. C. S. Morgan
5-6. ORNL - Y-12 Technical Library	56. J. F. Murdock
Document Reference Section	57. R. G. Niemeyer
7-26. Laboratory Records Department	58. S. A. Rabin
27. Laboratory Records, ORNL RC	59. R. E. Reed
28. ORNL Patent Office	60. R. G. Ross
29. R. J. Beaver	61. J. E. Savolainen
30. R. G. Berggren	62. O. Sisman
31. E. C. Bohlmann	63. I. Spiewak
32. J. Burka	64. R. L. Stephenson
33. F. L. Culler	65. J. O. Stiegler
34. J. E. Cunningham	66. J. A. Swartout
35. W. W. Davis	67. W. C. Thurber
36. J. H. DeVan	68. D. B. Trauger
37. J. H. Frye, Jr.	69. J. T. Venard
38. R. G. Gilliland	70. A. M. Weinberg
39. B. L. Greenstreet	71. J. R. Weir
40. G. Hallerman	72. W. J. Werner
41-45. M. R. Hill	73-92. G. D. Whitman
46. N. E. Hinkle	93. R. O. Williams
47. C. E. Larson	94. G. T. Yahr
48. C. F. Leitten, Jr.	95. A. A. Burr (consultant)
49. A. P. Litman	96. J. R. Johnson (consultant)
50. T. S. Lundy	97. C. S. Smith (consultant)
51. H. G. MacPherson	98. R. Smoluchowski (consultant)
52. W. R. Martin	

EXTERNAL DISTRIBUTION

99. M. R. Achter, Naval Research Laboratory
100. C. M. Adams, Jr.
101. Kenneth Antony, GE Evansdale
102. D. E. Baker, GE Hanford
- 103-104. D. F. Cope, ORO
105. Research and Development, ORO
106. M. A. Cordovi, International Nickel Company
107. Ersel Evans, GE Hanford
108. J. L. Gregg, Cornell University
109. J. E. Guthrie, Esso Research Engineering Company
110. H. E. Johnston, University of Alberta, Edmonton, Alberta, Canada
111. J. Simmons, AEC, Washington

- 112. E. E. Stansbury, University of Tennessee
- 113. D. K. Stevens, AEC, Washington
- 114. W. F. Zimmerman, GE (MSVD)
- 115-613. Given distribution as shown in TID-4500 (30th ed.)
under Metals, Ceramics, and Materials category