UNCLASSIFIED

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361048 4

ORNL-2243
Metallurgy and Ceramics
Cy. 4

ELECTROLESS-PLATED BRAZING ALLOYS

P. Patriarca
G. M. Slaughter
W. D. Manly

CENTRA
DOCU
LIBRAI
DO NOT TRAN
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
UCC
POST OFFICE BOX X · OAK RIDGE, TENNESSEE

UNCLASSIFIED

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, express 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 to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

ORNL-2243
Metallurgy and Ceramics
TID-4500 (12th ed.)

Contract No. W-7405-eng-26

METALLURGY DIVISION

ELECTROLESS-PLATED BRAZING ALLOYS

P. Patriarca, G. M. Slaughter, and W. D. Manly

DATE ISSUED

MAR 19 1957

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box X
Oak Ridge, Tennessee

UNCLASSIFIED

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0361048 4

ORNL-2243
Metallurgy and Ceramics
TID-4500 (12th ed.)

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Metallurgy Library
7. Reactor Experimental Engineering Library
8-27. Laboratory Records Department
28. Laboratory Records, ORNL R.C.
29. A. M. Weinberg
30. L. B. Emlet (K-25)
31. J. P. Murray (Y-12)
32. J. A. Swartout
33. E. H. Taylor
34. E. D. Shipley
35. M. L. Nelson
36. W. H. Jordan
37. C. P. Keim
38. R. S. Livingston
39. R. R. Dickison
40. S. C. Lind
41. F. L. Culler
42. A. H. Snell
43. A. Hollaender
44. M. T. Kelley
45. K. Z. Morgan
46. J. A. Lane
47. A. S. Householder
48. C. S. Harrill
49. C. E. Winters
50. D. S. Billington
51. D. W. Cardwell
52. E. M. King
53. A. J. Miller
54. D. D. Cowen
55. R. A. Charpie
56. M. J. Skinner
57. G. E. Boyd
58. P. M. Reyling
59. C. O. Smith
60. W. W. Parkinson
61. J. H. Frye, Jr.
62. W. D. Manly
63. J. E. Cunningham
64. G. M. Adamson
65. R. J. Beaver
66. E. S. Bomar, Jr.
67. J. H. DeVan
68. L. M. Doney
69. D. A. Douglas
70. R. J. Gray
71. J. P. Hammond
72. T. Hikido
73-93. M. R. Hill
94. E. E. Hoffman
95. L. K. Jetter
96. C. J. McHargue
97. R. B. Oliver
98-102. P. Patriarca
103. M. L. Picklesimer
104-108. G. M. Slaughter
109. G. P. Smith, Jr.
110. A. Taboada
111. H. L. Yakel, Jr.
112. E. Creutz (consultant)
113. N. J. Grant (consultant)
114. H. Leidheiser, Jr. (consultant)
115. T. S. Shevlin (consultant)
116. C. S. Smith (consultant)
117. E. E. Stansbury (consultant)
118. ORNL – Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

119. R. F. Bacher, California Institute of Technology
120. Division of Research and Development, AEC, ORO
121-498. Given distribution as shown in TID-4500 under Metallurgy and Ceramics category

ELECTROLESS-PLATED BRAZING ALLOYS

P. Patriarca G. M. Slaughter W. D. Manly

INTRODUCTION

A survey of the recent literature[1,2] reveals that modifications of the electroless nickel-plating process[3-5] effected by several industrial concerns have rendered the method economically feasible for commercial application. An obvious advantage of this method over the usual electroplating process is that a uniform plate can be deposited on a complex surface without the difficulties introduced by variations in "throwing power" of the electrolytic methods.

Briefly, the electroless nickel-plating process involves the deposition of a high-phosphorus nickel plate as a consequence of the reduction of a nickel salt to metallic nickel. A hypophosphite is converted to the phosphite with subsequent deposition of nickel in accordance with the simple reaction:

$$NiCl_2 + NaH_2PO_2 + H_2O \longrightarrow Ni + 2HCl + NaH_2PO_3$$

Since the nickel as deposited by this method has been reported[1,2] to contain from 5 to 10% phosphorus, secondary reactions probably play a significant role in the deposition mechanism.

Examination of the equilibrium phase diagram[6] of Fig. 1 will reveal that such nickel-phosphorus deposits constitute an elevated-temperature brazing alloy system of the simple eutectic type.

Of prime importance is the apparent possibility of using the electroless process to provide a very convenient method for preplacing this brazing alloy system so that it will be independent of the complexity of the assembly to be fabricated. Consideration of this possibility and interest in the Ni-P system in general led to the decision that a study of electroless nickel-base brazing alloys should be incorporated into an elevated-temperature brazing alloy development program.

Although the results of the preliminary studies conducted to date are limited in scope, they are believed to be significant and are therefore presented for the benefit of other researchers in the field of elevated-temperature brazing alloys.

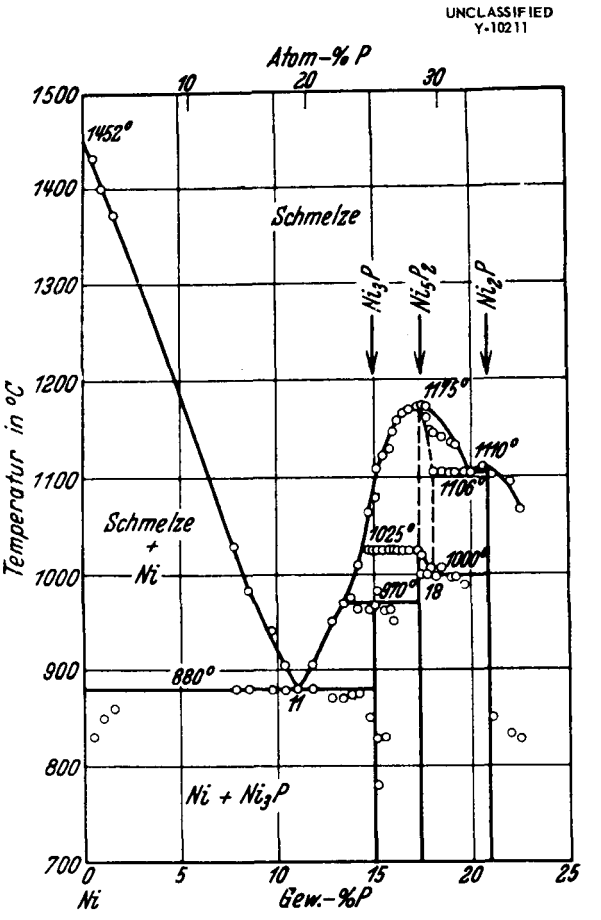

Abb. 388. Ni-P. Nickel-Phosphor.

Fig. 1. Nickel-Phosphorus Equilibrium Phase Diagram. (Reprinted from *Der aufbau der zweistofflegierungen*, by M. Hansen, Edwards Bros., Ann Arbor, 1943.)

[1] J. B. Campbell, "Electroless Nickel Plating: Where It Stands Today," *Materials and Methods* 37(5), 96 (1953).

[2] E. L. Gostin, "Electroless Plating Produces Hard Nickel Coating," *Iron Age* 171(24), 115 (1953).

[3] A. Brenner and G. E. Riddell, "Nickel Plating on Steel by Chemical Reduction," *J. Research Natl. Bur. Standards* 37, 31 (1946).

[4] A. Brenner and G. Riddell, "Deposition of Nickel and Cobalt by Chemical Reduction," *J. Research Natl. Bur. Standards* 39, 385 (1947).

[5] *Electroless Plating on Metals by Chemical Reduction*, National Bureau of Standards Technical Report 1097.

[6] M. Hansen, *Der aufbau der zweistofflegierungen*, Edwards Bros., Ann Arbor, 1943.

EXPERIMENTAL PROCEDURE AND RESULTS

To determine the feasibility of the use of this electroless Ni-P plate as a brazing alloy, a series of type 316 stainless steel strips $\frac{1}{2} \times 3 \times \frac{1}{16}$ in. were electroless-plated with a nominal thickness of 0.001 in. of Ni-P by procedures based on the method developed by the U. S. Bureau of Standards.

A photomicrograph of the Ni-P plate as deposited on the stainless steel is shown in Fig. 2. As may be noted, the plate is quite dense. An examination of the Vickers hardness indentations obtained with a Bergsman microhardness tester, at 25-g load, indicated that the plate was substantially hard (361 average) and brittle as evidenced by the shattering of the plate around the diamond indentation. This value, however, is somewhat less than the averages of 450 and 600 reported by industrial investigators.[1]

Standard flowability inverted-T joints were made by using a plated stainless steel strip as the horizontal member and an unplated stainless steel strip as the vertical member. This T-joint was tack-welded at the ends and brazed in a −70°F dew-point, hydrogen-atmosphere, globar-heated furnace at 1800°F for 10 min. Figure 3 shows a typical inverted-T joint brazed with electroless-deposited Ni-P. It may be noted that as the Ni-P plate melted, the melt sought the nearest capillary and adequately wet the unplated stainless steel member to form a uniform fillet along the full length.

The microstructure of the fillet is presented in Fig. 4, a photomicrograph at a magnification of 100X. Solution of the stainless steel members has taken place, contributing to the formation of primary crystals; these crystals can be seen along the walls and in the matrix of the fillet.

From Fig. 5, a photomicrograph, at a magnification of 1000X, of an area within the fillet of Fig. 4, the presence of a eutectic can be established. Hardness impressions of the larger, lighter, etching areas averaged 124 VHN, whereas the hardness of the darker etching matrix averaged 546 VHN. Although the chemical analysis of several Ni-P electroless deposits revealed a phosphorus content between 10 and 12%, the solution of stainless steel at 1800°F during the brazing operation had apparently shifted the composition of the brazed joint to a hypoeutectic. Further evidence to this effect exists in the

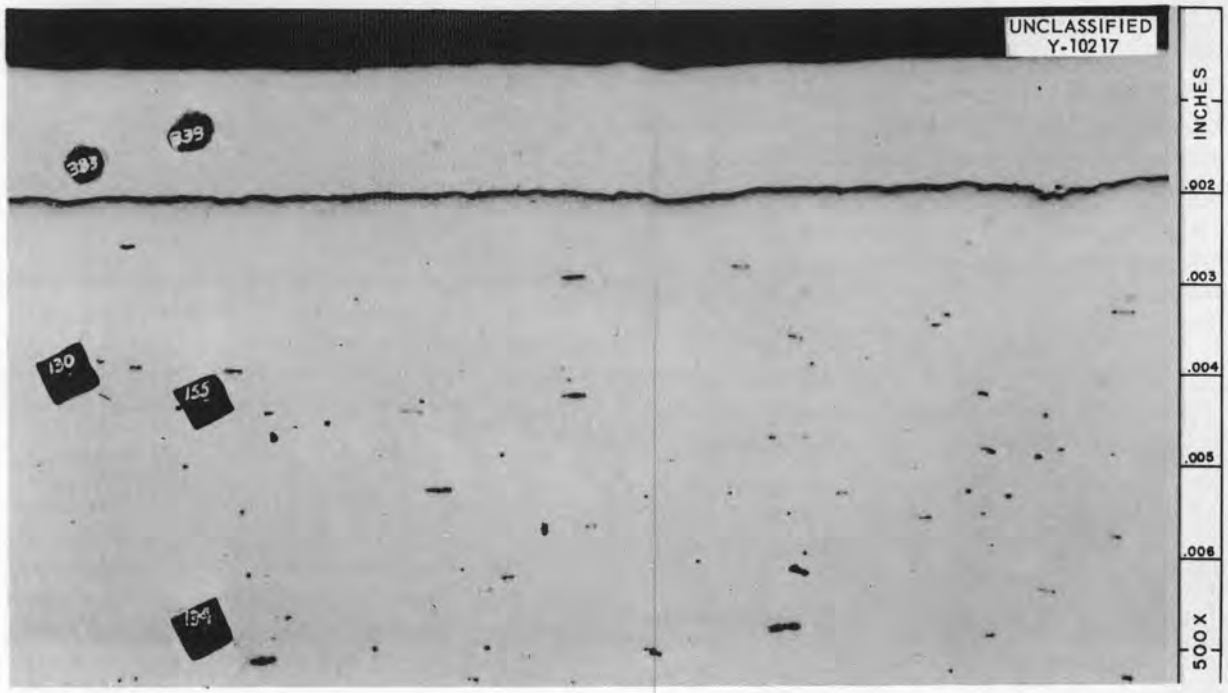

Fig. 2. Approximately 0.0014-in. Electroless Ni-P Plated on Type 316 Stainless Steel Illustrating the Density of the Plate and the Relative Hardness Between the Plate and the Stainless Steel. Unetched. 500X. Reduced 3%.

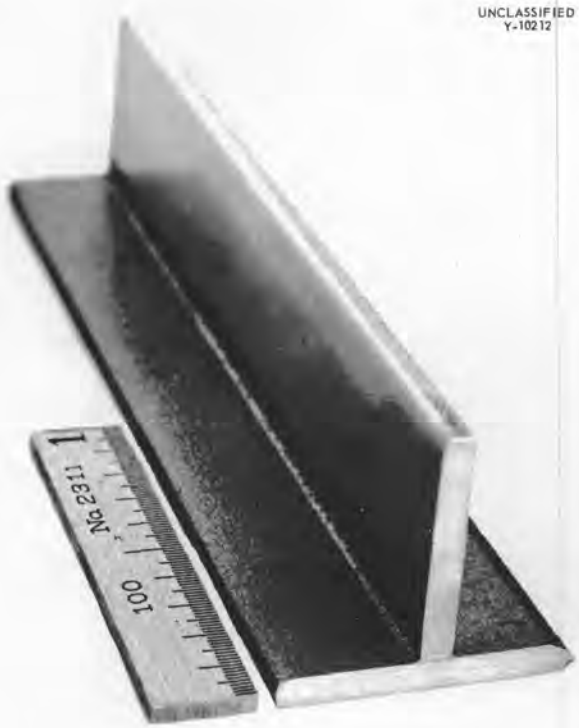

Fig. 3. As-Brazed Type 316 Stainless Steel Inverted-T Specimen Illustrating Excellent Flowability of the Electroless Ni-P Brazing Alloy.

photomicrograph of Fig. 6, taken at 750X magnification at a fillet–stainless steel interface. Excellent wetting occurred, as evidenced by the growth of primary crystals along the stainless steel. Their hardness corresponds to that exhibited by the lighter etching areas of Fig. 5. This would indicate that the solution of stainless steel by the Ni-P brazing alloy has resulted in a hypoeutectic composition consisting of an extensive solid solution of nickel, phosphorus, and type 316 stainless steel (wt %: 10 Cr–8 Ni–3 Mo–79 Fe) and a phase which may be a complex phosphide of the above elements.

Accordingly, a quantity of stainless steel sheet fins was prepared by punching holes with a nominal diameter of 0.190 in. in 0.010-in.-thick type 304 stainless steel sheet and leaving a lip sufficiently adequate to provide a 15-fin-per-inch spacing. These fins were plated with approximately 0.0015-in. electroless-deposited Ni-P brazing alloy on each surface and assembled with $^{3}/_{16}$-in.-OD, 0.020-in.-wall, type 316 stainless steel tubes into a small heat exchanger test specimen. Figure 7 is a photograph of this specimen after it was brazed at 1800°F for 10 min. Note that adequate flow, wetting, and filleting have occurred. One tube was sectioned for metallographic examination, a section of which is shown in Fig. 8. Examination of this photomicrograph indicates that preplacement of the electroless Ni-P brazing alloy in complex assemblies is feasible. It may be noted that the microstructure of the joint is similar to that observed in the basic inverted-T specimen of Fig. 4, as would be expected.

A portion of the sectioned tube-to-fin joint was then subjected to an oxidation test in static air at 1500°F for 100 hr. Results of this test are presented in Fig. 9, a photomicrograph of the joint after exposure. The extent of attack during this test was negligible. A section of an Inconel inverted-T specimen was then exposed to static air at 1500°F for 500 hr to further determine its oxidation resistance. The results of this test are presented in the photomicrograph of Fig. 10. Only minor attack was evident at the fillet-to-air interface.

A portion of an inverted-T specimen was submitted for static corrosion testing in sodium at 1500°F for 100 hr. Figure 11 is a photomicrograph of a section of the specimen after exposure. Metallographic examination of the specimen revealed the presence of small voids completely across the joint, indicating that the alloy would not be suitable for use in this type of environment.

These examinations made it apparent that the electroless-plated Ni-P alloy would not be adequate for joints requiring high-temperature resistance to sodium. The oxidation resistance of the alloy, however, appeared to be adequate for applications when the prime function of the brazing alloy would be to provide optimum heat-transfer characteristics.

EFFECT OF CHROMIUM ADDITIONS TO ELECTROLESS NICKEL

In an effort to improve the corrosion resistance of the electroless Ni-P brazing alloy in sodium, and, to a lesser extent, improve its resistance to oxidation, another series of test specimens was prepared. These type 316 stainless steel strips (similar to those used in the initial tests) were plated with approximately 0.001-in. electroless-deposited Ni-P and then, by means of conventional

electrodeposition, plated with approximately 0.0002 in. of chromium. A photomicrograph of a section of one such strip is shown in Fig. 12.

An inverted-T flowability specimen was made as described previously and brazed at 1800°F for 10 min in dry hydrogen. Excellent flow, wetting, and filleting were again observed, as shown in Fig. 13. The microstructure is somewhat different from that of the Ni-P fillet of Fig. 4, and this is attributable to the greater amount of chromium. Figure 14 shows the microstructure within the Ni-P-Cr stainless steel fillet at 750X magnification, revealing a coarser eutectic than that shown in Fig. 5.

Another portion of the inverted-T specimen was submitted for evaluation of corrosion resistance in sodium at 1500°F. The extent of attack after 100 hr of exposure is evident upon examination of Fig. 15. In this case the fillet remained relatively sound with decreased attack at the fillet-sodium interface. Examination of an Inconel test specimen exposed to static air at 1500°F for 500 hr revealed that the chromium addition to the electroless-plated Ni-P alloy had provided excellent oxidation resistance to the joint. This is shown in Fig. 16.

As would be expected, however, the phosphide portion of the eutectic rendered the fillet brittle and prone to cracking. This is illustrated in Fig. 17, a photomicrograph of a fillet of a T-joint after brazing. A higher magnification of the cracks in the brazing alloy microstructure of this fillet is shown in Fig. 18. The cracks are prevalent in the brittle phosphide phase (VHN approximately 500) and end abruptly upon reaching the softer nickel-rich primary phase.

It thus appears that the Ni-P-Cr alloy may be attractive in applications when resistance to either high-temperature air or molten sodium is imperative.

It is emphasized that this alloy should be used only when fracturing of the type described is not objectionable and when the base material is not notch sensitive to the extent that a braze metal fracture will propagate through the parent structure and cause premature failure.

CONCLUSIONS

As a result of this preliminary investigation the following conclusions may be drawn.

1. The electroless-plating process deposits an Ni-P brazing alloy that exhibits excellent wetability and flowability in conjunction with such high-temperature alloys as austenitic stainless steels or Inconel when heated above the eutectic temperature in a dry hydrogen atmosphere.
2. Complex tube-to-fin heat exchanger assemblies can be fabricated by preplating with electroless Ni-P alloy and then brazing at 1800°F in dry hydrogen.
3. Electroless Ni-P brazed type 316 stainless steel and Inconel joints exhibit favorable oxidation resistance after exposure to air at temperatures up to 1500°F for extended periods of time.
4. Electroless Ni-P brazed type 316 stainless steel joints exhibit poor corrosion resistance to sodium when exposed at 1500°F for 100 hr.
5. The addition of chromium to the Ni-P brazing alloy by electrodeposition provides a means for ensuring excellent oxidation resistance of the fillet.
6. The resistance to sodium attack of the electroless Ni-P brazing alloy can be significantly improved by the addition of chromium by electrodeposition.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contribution of E. N. Skinner of the International Nickel Company, who recommended that a study be conducted to determine the use of electroless nickel as a brazing alloy.

The authors also wish to acknowledge the services of R. J. Gray and the members of the Metallographic Section of the ORNL Metallurgy Division for the metallography contained herein, and thanks are due E. E. Hoffman of the General Corrosion Section for his cooperation in conducting the corrosion studies.

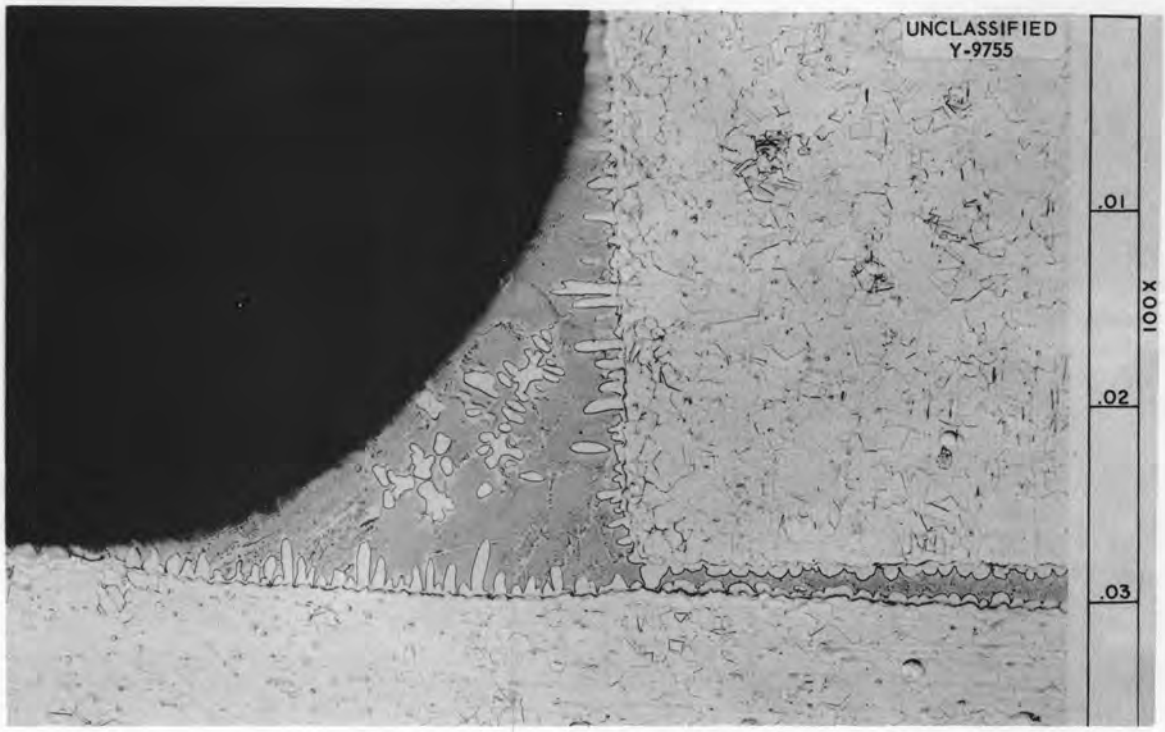

Fig. 4. Section of the T-Specimen Shown in Fig. 3 Illustrating the Microstructure of the Electroless Ni-P Brazed Type 316 Stainless Steel Joint After It Was Brazed at 1800°F in Dry Hydrogen for 10 min. Etched with glyceria regia. 100X.

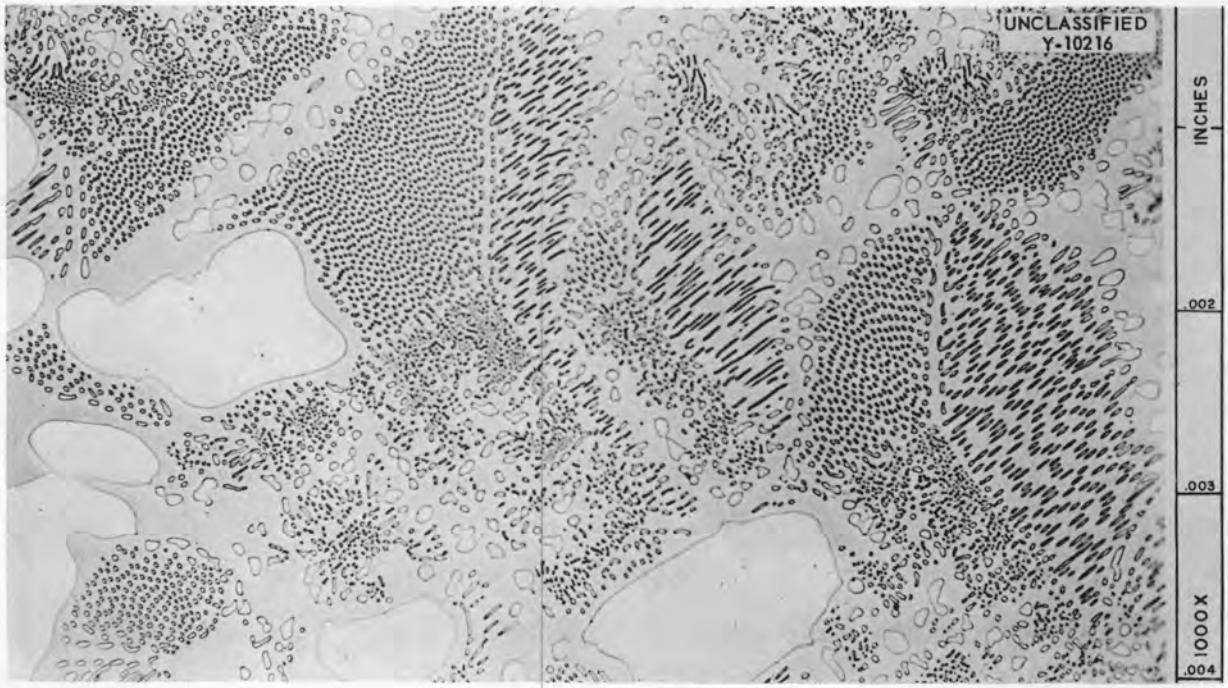

Fig. 5. Microstructure of the Electroless Ni-P Brazing Alloy Within the Fillet of Fig. 4 Indicating the Presence of a Eutectic. Etched with glyceria regia. 1000X. Reduced 3%.

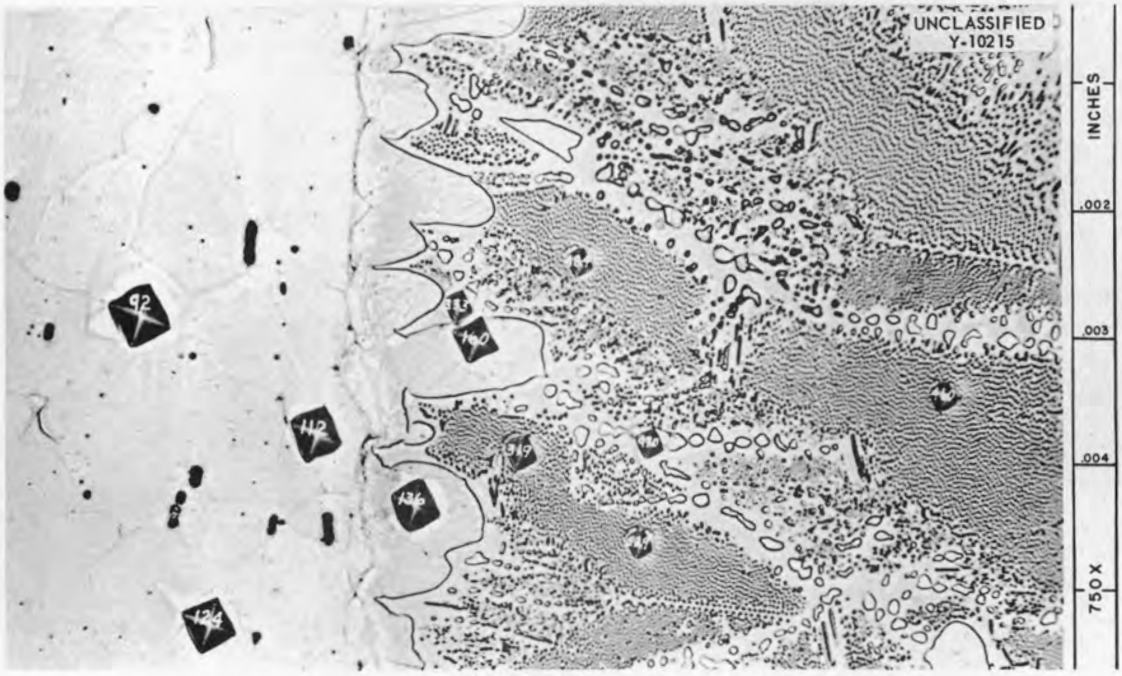

Fig. 6. Microstructure of the Electroless Ni-P Brazing Alloy at the Fillet–Base-Metal Interface Illustrating the Growth of Relatively Soft Primary Crystals from the Stainless Steel. Etched with glyceria regia. 750X. Reduced 11.5%.

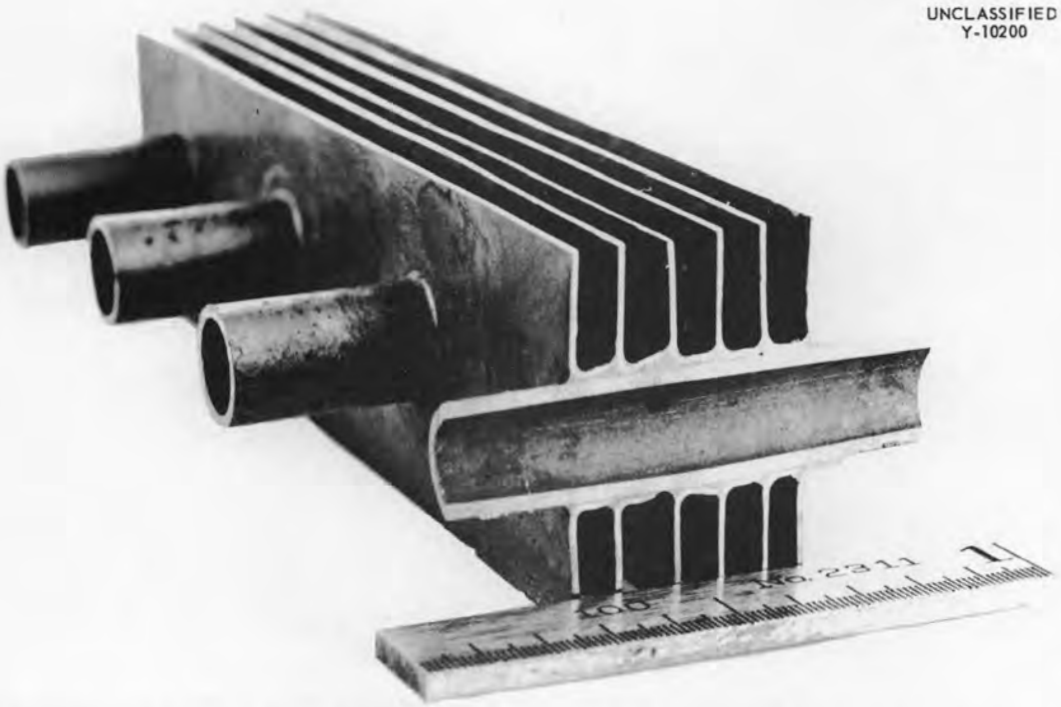

Fig. 7. Tube-to-Fin Test Specimen Fabricated by Assembly of Preplated Type 304 Stainless Steel Fins and Type 316 Stainless Steel Tubes Followed by Brazing at 1800°F in Dry Hydrogen.

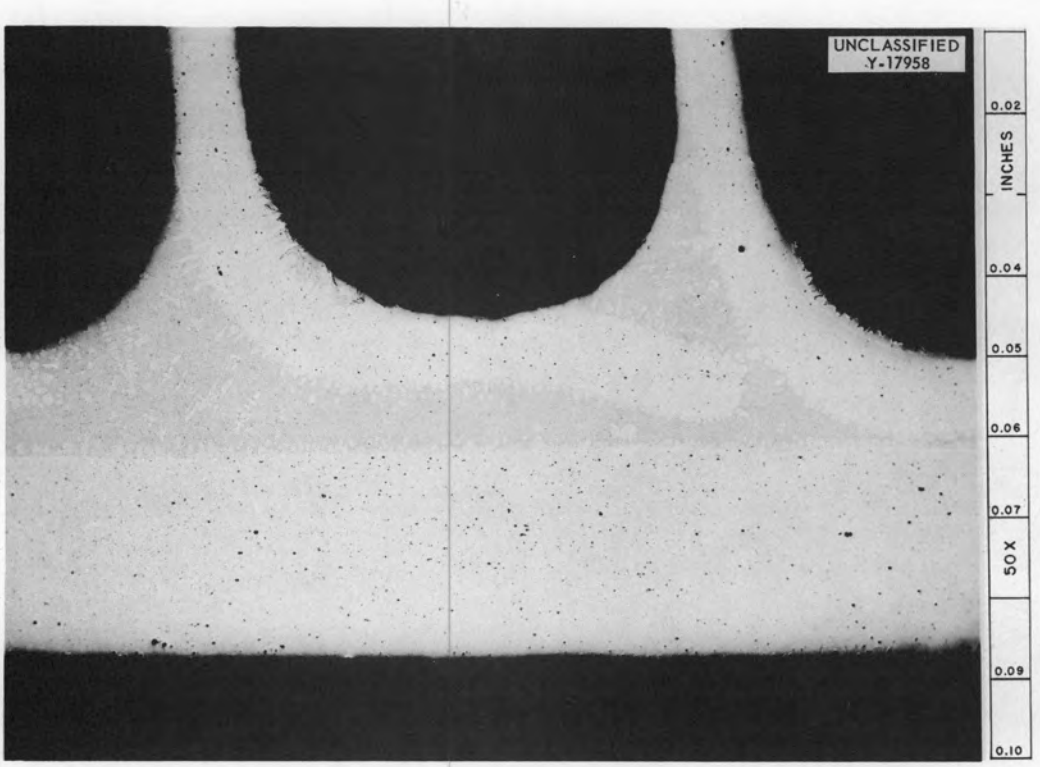

Fig. 8. Section of the Tube-to-Fin Assembly Shown in Fig. 7 Illustrating the Feasibility of Tube-to-Fin Fabrication by the Preplate Method. Etched with glyceria regia. 50X. Reduced 15%.

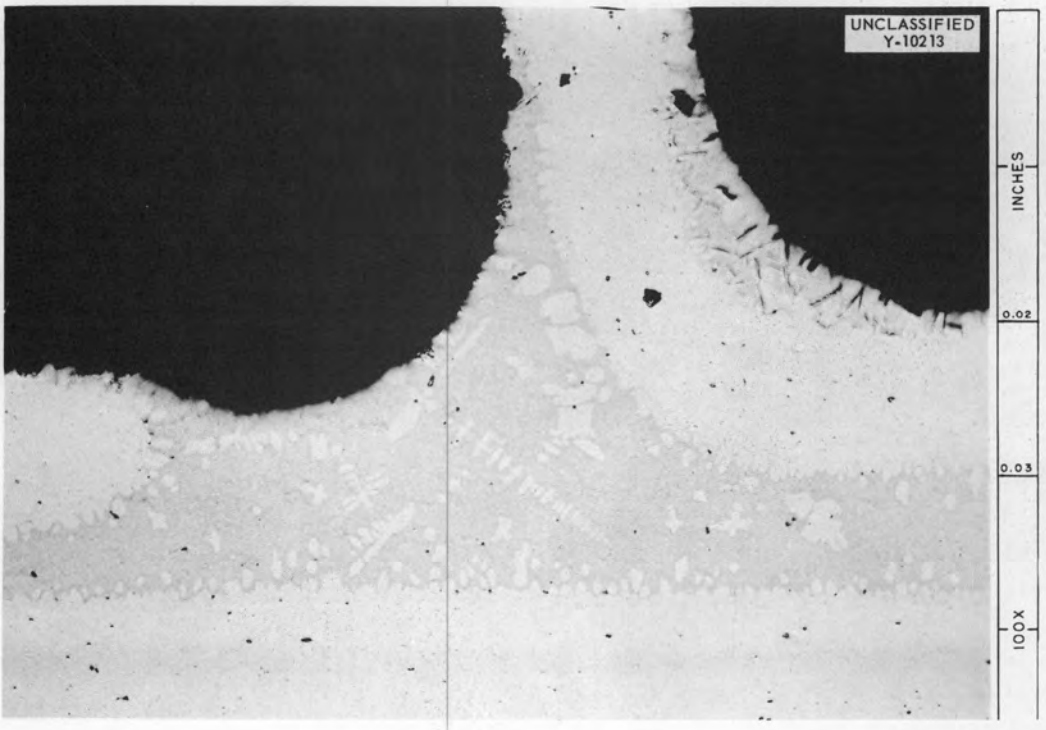

Fig. 9. Section of Tube-to-Fin Joint Illustrated in Fig. 8 After Exposure to Static Air at 1500°F for 100 hr. Etched with glyceria regia. 100X. Reduced 17%.

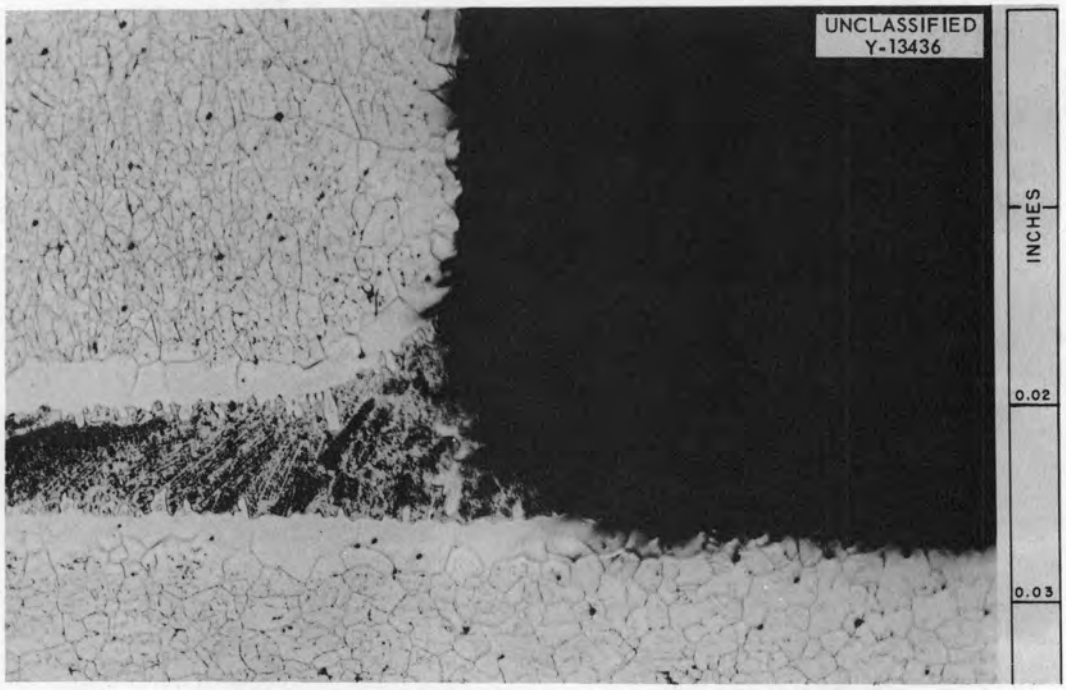

Fig. 10. Inconel T-Joint Brazed with Electroless Ni-P and Held for 500 hr at 1500°F in Static Air. Etched with glyceria regia. 100X.

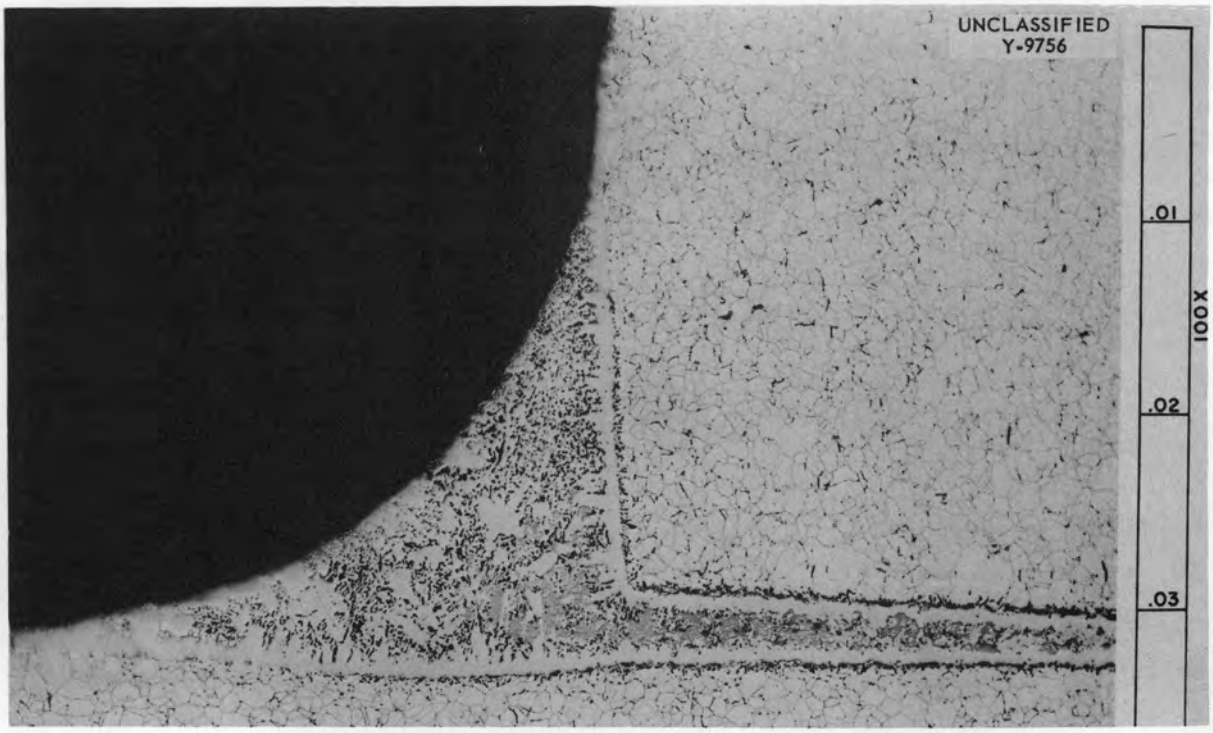

Fig. 11. Photomicrograph of the Electroless Ni-P Brazed Type 316 Stainless Steel Joint After Exposure to Sodium at 1500°F for a Period of 100 hr. Etched with glyceria regia. 100X.

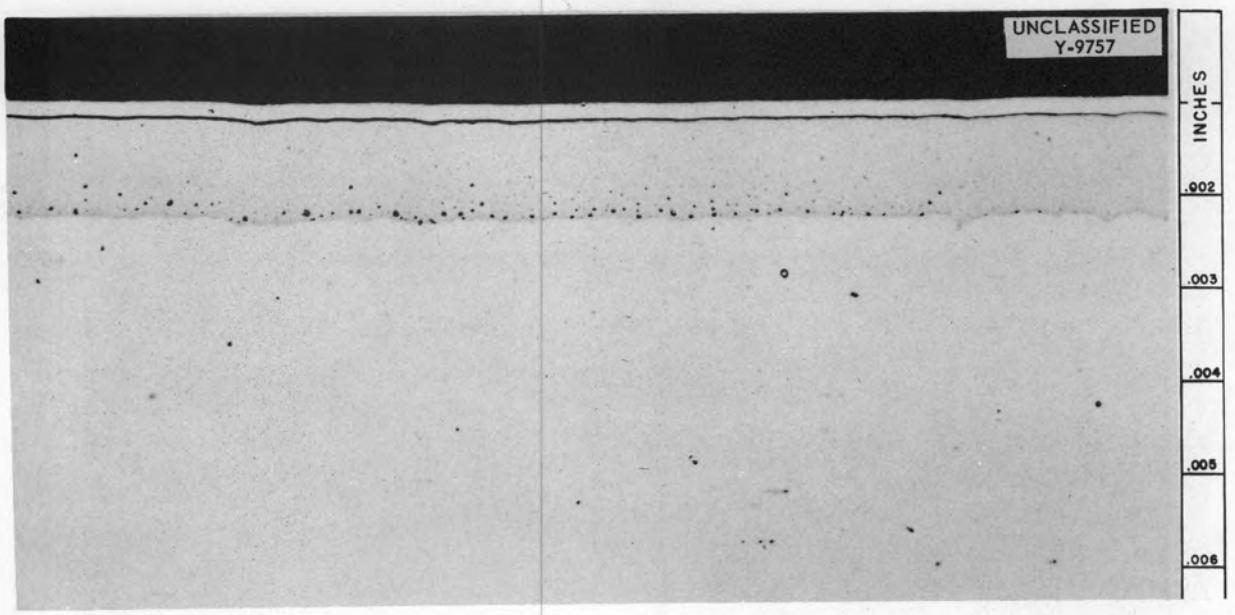

Fig. 12. Approximately 0.0002-in. Electrolytic Chromium on 0.001-in. Electroless Ni-P as Deposited on Type 316 Stainless Steel. Unetched. 500X. Reduced 3%.

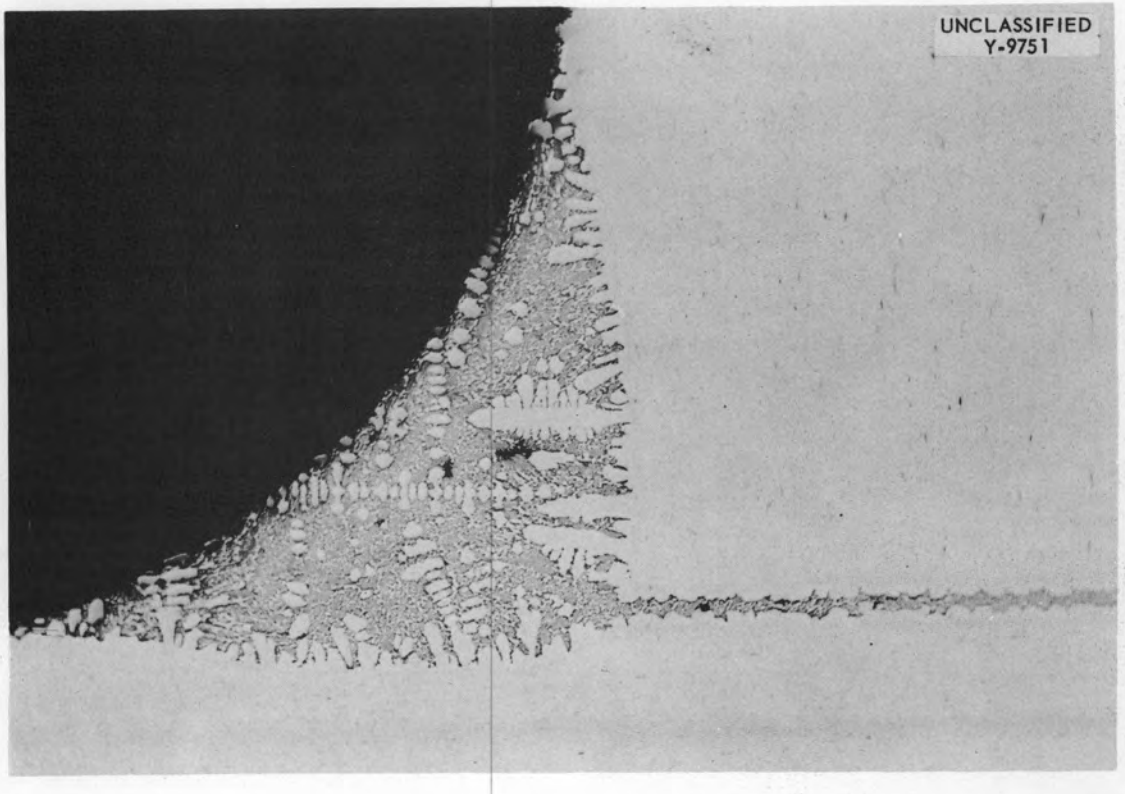

Fig. 13. Microstructure of an Ni-P-Cr Brazed Type 316 Stainless Steel Joint as Brazed at 1800°F in Dry Hydrogen for 10 min. Etched with glyceria regia. 100X.

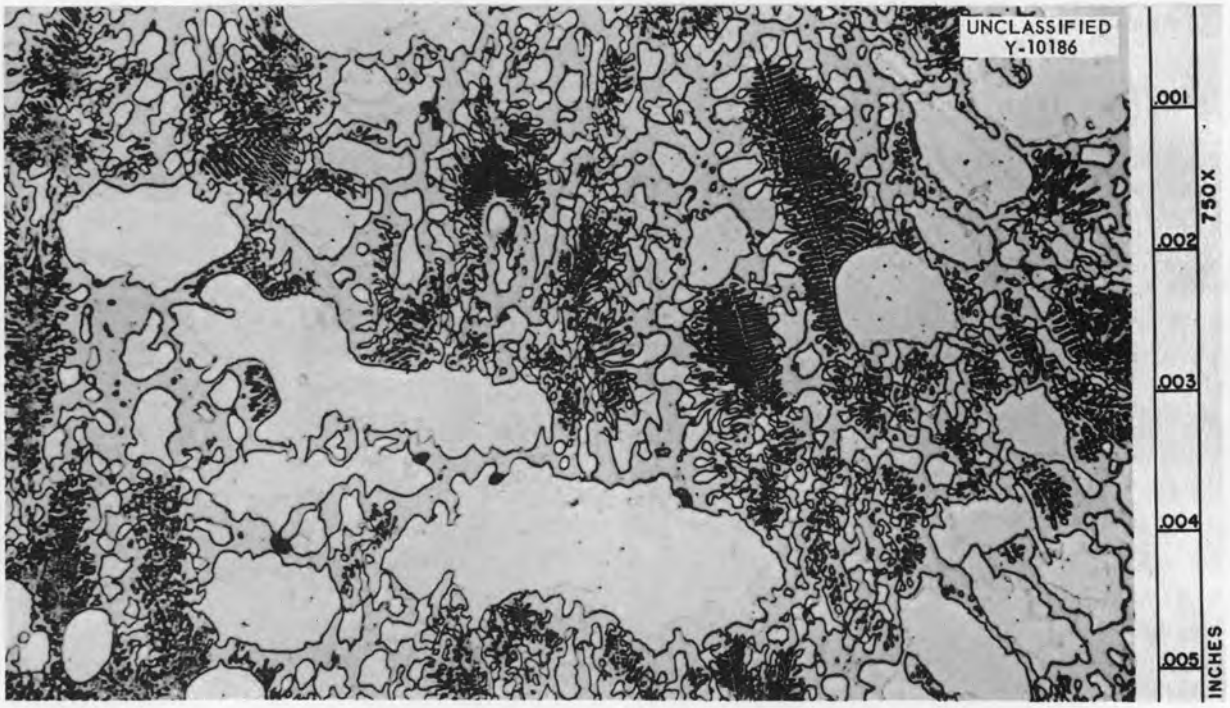

Fig. 14. Microstructure of the Ni-P-Cr Brazing Alloy Within the Fillet of Fig. 13 Indicating the Presence of a Eutectic. Etched with glyceria regia. 750X. Reduced 2%.

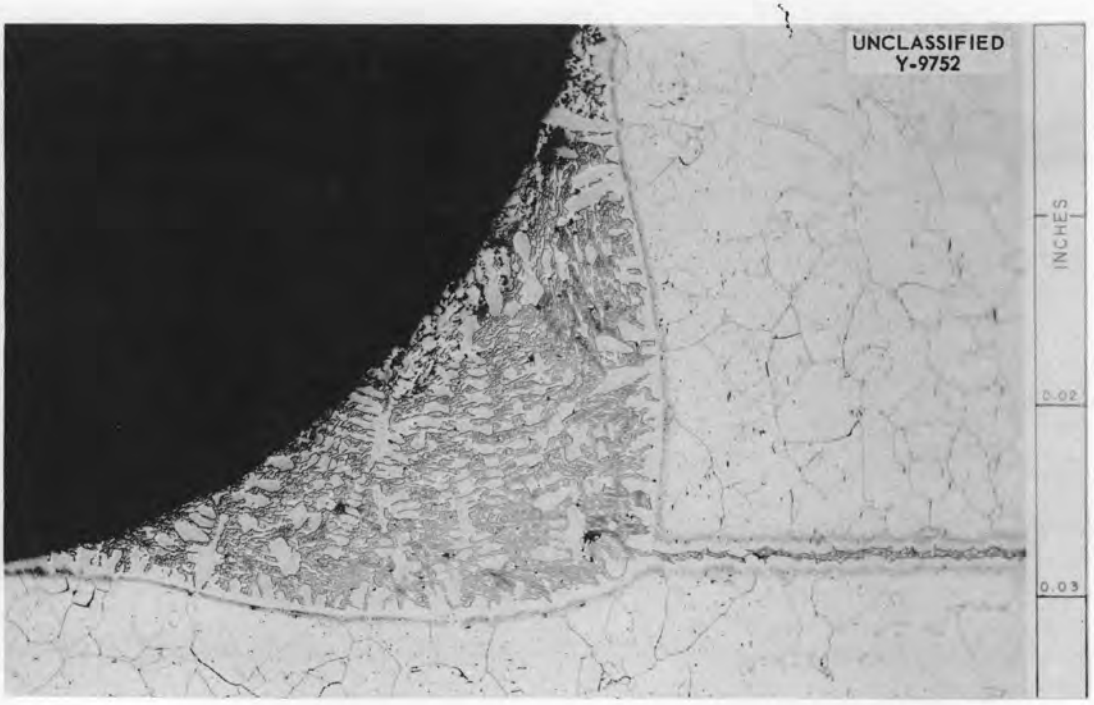

Fig. 15. Photomicrograph of the Ni-P-Cr Brazed Type 316 Stainless Steel Joint After Exposure to Sodium at 1500°F for a Period of 100 hr. Etched with glyceria regia. 100X.

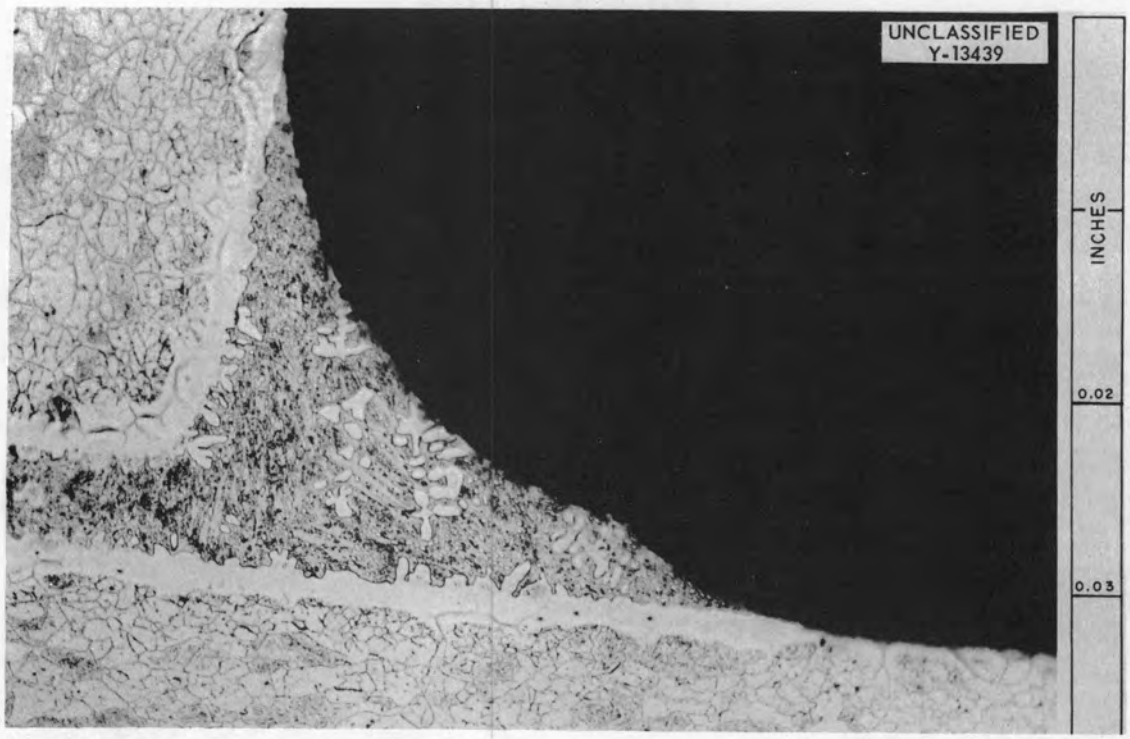

Fig. 16. Inconel T-Joint Brazed with Ni-P-Cr and Held for 500 hr at 1500°F in Static Air. Etched with glyceria regia. 100X.

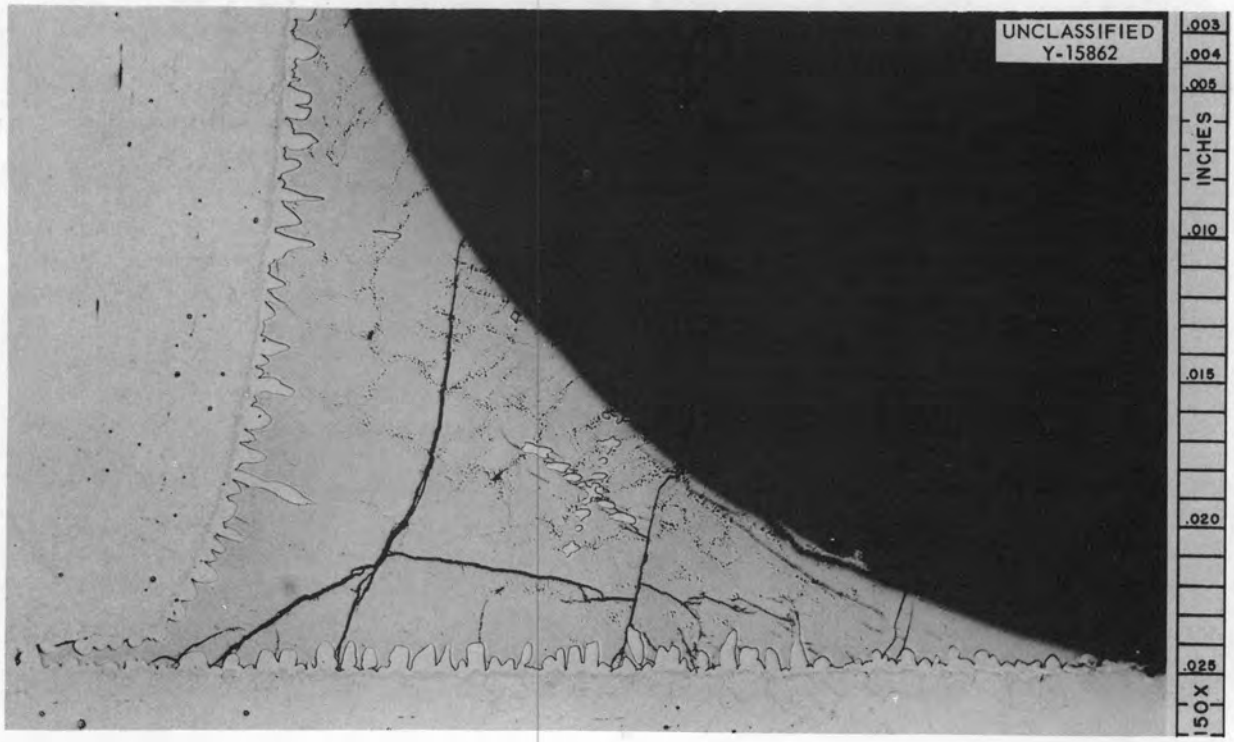

Fig. 17. Photomicrograph of an Inconel T-Joint Brazed with Electroless Nickel in the As-Brazed Condition. Note the cracks which are prsent in the braze fillet. Electrolytically etched in oxalic acid. 150X.

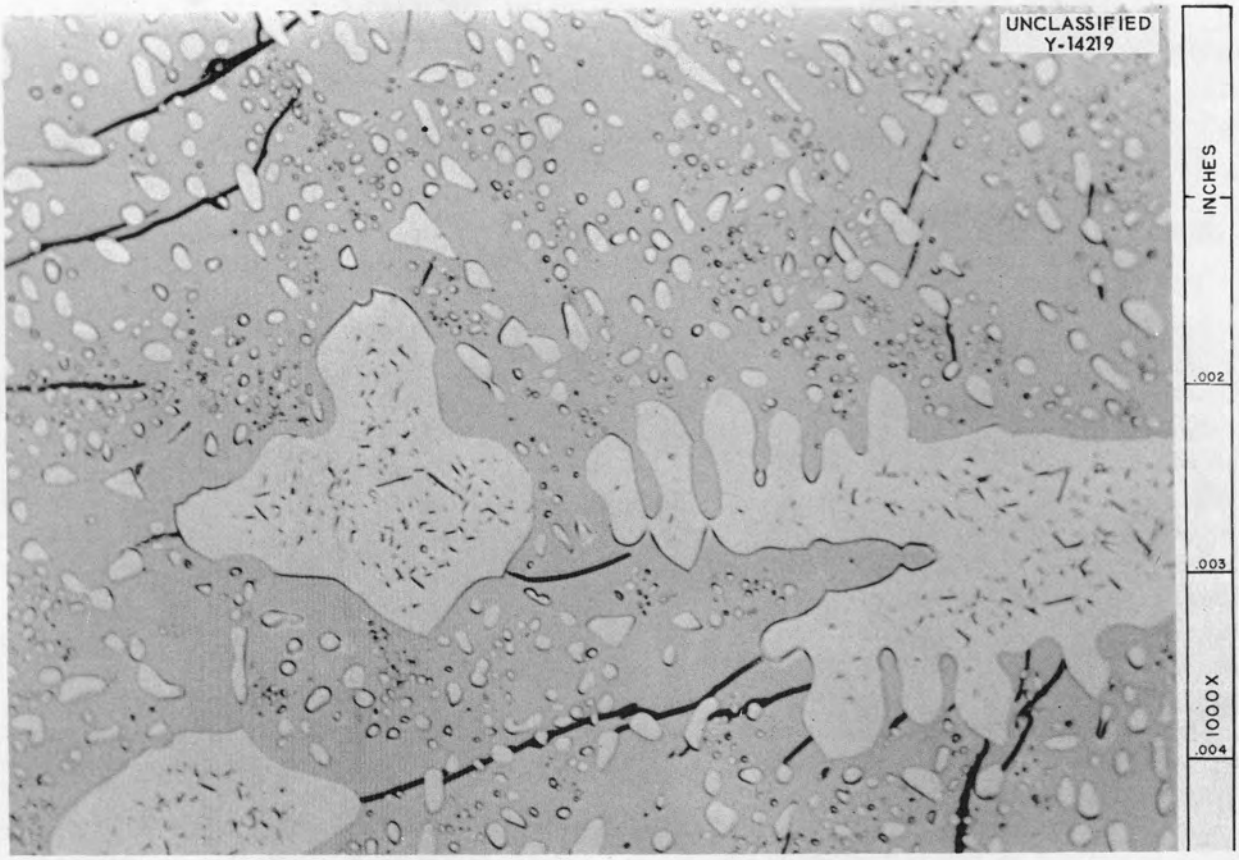

Fig. 18. Photomicrograph of the Electroless Nickel Brazing Alloy at High Magnification. Note the cracks which occurred in the brittle phosphide phase. Electrolytically etched in oxalic acid. 1000X. Reduced 3%.