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ABSTRACT

The feasibility of using electroless nickel, a chemical deposit containing about 10 wt % phosphorous in nickel, as the brazing alloy for assembling tubular stainless steel fuel elements of the type specified in Core I of the N. S. Savannah was investigated. This material was selected primarily because of the ease of braze-metal preplacement by chemical deposition of the alloy on type 304 stainless steel ferrule spacers, prior to fuel-bundle assembly. Brazed joints produced by this method were generally characterized by a relatively ductile solid-solution region at the thinnest portions of the fillet. This ductile zone should minimize the possibility of complete propagation of hairline cracks, which form in the brittle, eutectic regions of fillet. The microstructural appearance of the electroless-nickel joints was not appreciably affected by variations in the brazing temperature from 1750 to 1900°F or the brazing time from 15 to 60 min.

Several plating solutions were evaluated and all were found to be capable of producing deposits suitable for brazing applications. Corrosion tests conducted in static 525°F water indicated that no significant

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attack of joints brazed with electroless nickel had occurred after 300-hr exposure. A small fuel bundle was successfully assembled by brazing with electroless nickel.

I. INTRODUCTION

Core I fuel elements for the N. S. Savannah pressurized-water nuclear power plant have been designed, and are being constructed by the Babcock and Wilcox Company. The reference design for these elements specifies that forty-one tubes of type 304 stainless steel, 6 ft long x 0.500-in. OD x 0.430-in. ID, containing slightly enriched UO_2 pellets will be assembled into a rigid bundle by brazing. Spacing between the individual fuel tubes in the subassembly is effected by the use of 1-in.- and 1.5-in.-long type 304 stainless steel tubular ferrules brazed at approximately 8-in. intervals along the length of the fuel tubes. Four subassemblies are mechanically attached to form a complete fuel element. The essential features of the reference design are illustrated in Fig. 1 (ORNL-LR-DWG 33924). Although some design changes have been made, this schematic drawing delineates the basic geometry of an N. S. Savannah fuel element. The binding strips indicated in this figure have been replaced by peripheral ferrules.

Microbraz No. 50,¹ a nickel-base brazing alloy having the nominal composition 10 wt % phosphorous, 13 wt % chromium, 0.15 wt % (max) carbon, and balance nickel, was initially selected as the reference brazing alloy. To validate this material selection, the Babcock and Wilcox Company conducted a test program designed to develop production brazing procedures for full-size fuel bundles. It was learned from Babcock and Wilcox Company personnel² that assembly of developmental fuel elements required up to 36 hr with most of the assembly time being used to appropriately preplace the powdered brazing alloy. The magnitude of this task can be appreciated from the fact that 450 ferrules of various sizes are presently specified for each reference subassembly, and 184,320 brazed joints are required in the entire fuel loading.

¹Wall-Colmonoy Corporation, Detroit, Michigan.

²Private communication from H. Lange, Babcock and Wilcox Company, Lynchburg, Virginia.

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SECTION A-A

Fig. 1. Merchant Ship Reactor Brazed Fuel Bundle.

In view of the laborious task of bundle assembly, the Metallurgy Division of the Oak Ridge National Laboratory undertook, as a part of its total effort in support of the Maritime Reactors Branch, a modest brazing program designed to determine the suitability of an alternate brazing alloy which would be more amenable to production assembly.

The alloy selected for consideration was electroless nickel. This brazing alloy is obtained by chemical deposition of a nickel-base material on the desired surface. The deposit or plate contains a quantity of phosphorous which is sufficient to lower the melting range to temperatures suitable for the controlled-atmosphere brazing of stainless steel and nickel-base alloys. The peculiar advantage of this material with respect to brazing of fuel bundles is that the alloy can be preplaced on the ferrules by chemical plating prior to fuel bundle assembly. The assembly operation is consequently reduced to building up the required structure from the component parts in a brazing jig.

This report describes the work performed to date at ORNL to determine the feasibility of using electroless nickel in N. S. Savannah fuel elements.

II. REVIEW OF PREVIOUS WORK

Electroless-nickel plating is a process in which nickel is deposited on certain catalytic surfaces from a nickel salt-hypophosphite solution without the use of an electric current. These deposits are not pure nickel but contain from 6 to 11 wt % phosphorous. Since the deposition is chemical rather than electrolytic in nature, coatings of uniform thickness can be produced in recessed areas, as well as on exposed surfaces and corners.

This process was discovered fortuitously by A. Brenner and G. Riddell in 1946 at the National Bureau of Standards while attempting to develop a bath for electrodepositing tungsten alloys.³ Electroless-nickel plating baths as developed by Brenner and Riddell consist of aqueous solutions of nickel salts; hypophosphite ions, which are the active chemical-reducing agents; and a hydroxyacetate, which serves as a complexing or buffering agent. The chemical reactions involved in the plating process are as follows:³

³A. Brenner and G. Riddell, "Electroless Plating Comes of Age," Metal Finishing 52(11), 68 - 76 (November, 1954).

Reaction (1) provides the nickel deposition. Since an acid is formed, the buffering agent is required to prevent rapid changes in the pH of the bath, and also to keep the metal salts in solution. Reaction (2) occurs concurrently with the reaction (1) and represents waste of reducing power. Because of this side reaction, the deposition of nickel is only 37% efficient with respect to the hypophosphite ion concentration in the plating solution.

Although the deposits produced from these solutions are hard and smooth, the deposition rate is quite low, being on the order of 0.5 mil/hr. The baths are also prone to spontaneous decomposition, with the nickel in solution being precipitated in the plating vessel instead of being deposited on the catalytic surfaces. In general, these solutions are not suitable for commercial applications requiring deposition of electroless nickel in adherent deposits at high plating rates.

In 1953, G. Gutzeit and E. J. Ramirez developed a bath that utilized certain "exaltants" to increase the deposition rate and retard spontaneous bath decomposition.⁴ These "exaltants" are saturated aliphatic dicarboxylic acids of which succinic acid seems to provide the best results. Such "exalted" baths exhibit deposition rates of 1.5 mil/hr and are highly stable. General American Transportation Corporation, who holds the patents for this process, is presently doing large-scale continuous-process electroless plating under the trade name of "Kanigen."

Electroless nickel is promising as a high-temperature brazing alloy, because it (1) can be uniformly deposited in complex shapes, and (2) the phosphorous contained in the deposit produces a hypoeutectic alloy having a reasonably low-melting range. One of the earliest studies employing electroless nickel as a brazing alloy was conducted at the Oak Ridge National Laboratory.⁵ Inverted-T specimens of austenitic stainless steels and Inconel were plated with approximately 1 mil of electroless nickel and heated to 1800°F in dry hydrogen. Sound joints were obtained and the flow and wetting characteristics of the alloy were excellent. Complex tube-to-fin heat exchanger assemblies were also brazed with satisfactory results.

⁴G. Gutzeit and E. S. Ramirez, Assignors to General American Transportation Corporation, Process of Chemical Nickel Plating and Bath therefore, U. S. Patent 2,658,842 (November 10, 1953).

⁵P. Patriarca et al., Electroless-Plated Brazing Alloys, ORNL-2243 (March 19, 1957).

A powdered brazing alloy having a composition essentially the same as electroless nickel is marketed by the Wall-Colmonoy Corporation under the trade name Microbraz No. 10.

III. PLATING STUDIES

The first portion of the present program involved an evaluation of several available plating solutions in terms of rate of deposition, visual appearance of the deposit, and chemistry of the resultant plate. The phosphorous content of the plate, of course, dictates the flow temperature and microstructural make-up of the braze metal. It has been pointed out by Ziehlke et al.,⁶ that considerable variation exists in the phosphorous content of commercial electroless-nickel plate. These investigators cited phosphorous assays of 7.2 wt % - 10.3 wt % on plates obtained from different vendors. As can be determined from the nickel-phosphorous constitution diagram shown in Fig. 2 (Y-29717), these variations in phosphorous mean that the liquidus temperature of the braze metal can vary from about 1690°F to 1870°F and the brazing alloy can contain from 6 to 35% of the ductile primary nickel phase. The implications in terms of required brazing temperature and mechanical properties of the brazed joint are obvious.

Four plating solutions listed in Table I were studied. Each solution contains nickel cations, hypophosphite anions, and an organic salt to control the pH. In the plating investigation, 2-in. squares of 0.015-in.-thick type 304 stainless steel were plated in each solution for times varying from 1/2 to 2-1/2 hr. Electroless nickel was deposited on only one surface; the other surface being masked with pressure-sensitive tape. Prior to plating, each sheet was prepared by the following procedure: (1) abrade surface with 600-grit paper, (2) degrease with acetone and air dry, (3) anodic etch in 37% HCl for 1 min using a nickel cathode, (4) nickel strike at 70°F for 2 min in a solution containing 200 g/liter of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 93 ml/liter of concentrated HCl, (5) rinse in water, (6) dip in 37% HCl for 30 sec, and (7) rinse in water.

The specimens were plated immediately after the outlined cleaning procedure. During plating which was performed in a static bath, the solution was maintained at a temperature of 185 - 205°F and a pH of 4 - 5. Periodic pH adjustments were made by addition of a mild, sodium hydroxide solution to the plating bath.

⁶K. T. Ziehlke et al., The Heat Treatment of Electroless-Nickel Coatings, K-1308 (February 2, 1959).

Y-29717

Fig. 2. Nickel-Phosphorous Constitution Diagram.

TABLE I

PLATING SOLUTIONS FOR ELECTROLESS NICKEL

Solution No. 1	
<u>Acetate-Chloride</u>	
Nickel Chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	21 g/liter
Sodium Hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	24 g/liter
Sodium Acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$)	10 g/liter
Solution No. 2	
<u>Acetate-Sulfate</u>	
Nickel Sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$)	30 g/liter
Sodium Hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	10 g/liter
Sodium Acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$)	10 g/liter
Solution No. 3	
<u>Glycolic Acid-Chloride</u>	
Nickel Chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	30 g/liter
Sodium Hydroxide (NaOH)	21 g/liter
Sodium Hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	500 g/liter ^a
Glycolic Acid ($\text{C}_2\text{H}_4\text{O}_3$)	correct to pH = 6
Solution No. 4	
<u>Succinate-Chloride</u>	
Nickel Chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	22 g/liter
Sodium Hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	30 g/liter
Sodium Succinate ($\text{Na}_2\text{C}_4\text{H}_4 \cdot 6\text{H}_2\text{O}$)	15 g/liter

^aA separate solution was prepared, 20 cc of which was added at the start of plating and 4 cc additional after each half-hour at plating.

A portion of each of the plated stainless squares was used for metallographic measurement of the thickness of the electroless deposit. The electroless plate was mechanically stripped from another portion of each sample and submitted for analytical determination of the phosphorous content. Results of these plate-thickness measurements and phosphorous determinations for the four plating solutions listed in Table I are summarized in Table II. Data are presented for two different runs with Solution No. 4 (succinate-chloride). The difference between Run A and Run B is that in the latter run, two separate plating solutions were used with one being filtered and reheated while the other was in use. Filtering of the solutions was required to remove particulate matter from the bath and minimize the amount of spontaneous decomposition. It can be seen from the data presented in Table II that the average deposition rate was highest for the succinate-chloride solutions. After 2-1/2 hr of plating, the thickness of the electroless deposit varied from 0.40 mil with Solution No. 3 to 0.93 mil with Solution No. 4 (Run B). The analyzed phosphorous contents of the various samples showed a generally random variation with time and ranged from 9.1 to 11.9 wt %.⁷ The higher deposition rates and more varied phosphorous assays previously cited as typical of commercial practice may result from the widespread use of recirculating systems.

Photomicrographs of cross sections through representative plated specimens are shown in Figs. 3 (Y-27456) and 4 (Y-27461). Figure 3 illustrates the deposit obtained from Solution No. 1 after 2 hr of plating while Fig. 4 shows the deposit obtained with Solution No. 4, Run A, for the same period. The typical laminated appearance of the amorphous deposit is apparent in each case and little difference can be discerned in the quality of the two deposits. In the subsequent brazing studies, Solution No. 4 was generally used since it was less prone to spontaneous decomposition.

IV. BRAZING STUDIES

The brazing studies, per se, involved two general types of investigations. One was a series of metallographic studies on the effect of various brazing cycles and post-braze heat treatments on the quality of brazed joints; the

⁷Qualification of the analytical method with a reference from the National Bureau of Standards indicated that inaccuracies were < 1% of the total phosphorous content.

TABLE II

EFFECT OF PLATING TIME ON PHOSPHOROUS CONTENT
AND THICKNESS OF ELECTROLESS-NICKEL DEPOSITS

Solution	Time-Dependent Variable	Plating Time					Average Deposition Rate mil/hr
		1/2 hr	1 hr	1-1/2 hr	2 hr	2-1/2 hr	
No. 1	Thickness(mils)	0.25	0.42	0.50	0.55	0.54	0.22
	wt % P	9.3	10.4	--	11.1	--	--
No. 2	Thickness(mils)	0.25	0.48	0.46	0.56	0.55	0.22
	wt % P	11.6	11.8	11.9	10.8	10.7	--
No. 3	Thickness(mils)	nil	nil	0.05	0.18	0.40	0.16
	wt % P	--	--	--	11.4	11.8	--
No. 4 Run A	Thickness(mils)	0.25	0.34	0.64	0.69	0.78	0.31
	wt % P	10.2	10.8	11.2	11.9	10.8	--
No. 4 Run B	Thickness(mils)	0.16	0.42	0.57	0.69	0.93	0.37
	wt % P	--	9.1	--	10.6	10.8	--

Y-27456

Fig. 3. Electroless-Nickel Plate on Type 304L Stainless Steel Obtained After 2-Hr Immersion in Solution No. 1 (Acetate-Chloride). Etchant: 10% CrO_3 , electrolytic.

Y-27461

Fig. 4. Electroless-Nickel Plate on Type 304 Stainless Steel Obtained After 2-Hr Immersion in Solution No. 4, Run A (Succinate-Chloride). Etchant: 10% CrO_3 , electrolytic.

second was an evaluation of the effects of various brazing cycles on the mechanical properties of the brazed joints. Results of studies are summarized in the following sections.

A. Metallographic Investigation

To determine the effect of brazing cycle on the general nature of electroless-nickel brazed joints, with particular reference to whether or not the particle size and distribution of the brittle Ni_3P phase could be varied, a series of three-ply sandwiches were prepared and brazed in dry hydrogen. The 2-in.-square sandwiches consisted of two type 304L stainless steel cover sheets 0.015 in. thick plated on one side with approximately 0.7 mils of electroless nickel and bonded to a center piece of 0.2-in.-thick type 304 stainless steel. Specimens were brazed at 1750, 1800, 1850, and 1900°F for 15, 30, and 60 min. Metallographic examination of these 12 samples indicated no consistent time- and temperature-dependent effects in terms of size and distribution of the Ni_3P phase. In every case, however, sound continuous bonds were produced, and alloying with the base-metal (undercutting) to significant depth did not occur. A typical bond obtained in this experiment is illustrated in Fig. 5 (Y-28558).

In view of the minor influence of these variations in brazing cycle (time and temperature), it was decided to determine the effects of a post-braze heat treatment on the distribution of the brittle phase. A treatment similar to that used to spheroidize Fe_3C in steel was studied in which specimens were held for various times just below the eutectic temperature. Three samples taken from the specimen brazed for 15 min at 1800°F were held at 1560°F for 1, 3, and 5 hr, respectively. Metallographic examination again revealed no significant and consistent microstructural alterations.

One other experiment was conducted with the three-ply sandwiches. In this experiment two samples were brazed under identical conditions, 30 min at 1850°F, except that one specimen was allowed to furnace cool from the brazing temperature while the other specimen was pulled into the cold zone of the furnace and allowed to rapidly dissipate its heat. Portions of each of these samples were subsequently held for 6 and 12 hr at 1560°F. From metallographic study it appeared that the Ni_3P phase in the slowly cooled specimen had a slightly more favorable distribution being present as small, discontinuous, spherical particles. No additional improvements were realized with the more extended heat treatments.

Y-28558

Fig. 5. Appearance of Electroless-Nickel Bond Between Type 304 and 304L Stainless Steel Sheets Obtained by Brazing for 15 Min in H_2 at 1800°F. Etchant: 5% CrO_3 , electrolytic.

In addition to the sandwich-type specimen, attention was directed to the metallographic examination of tube-to-ferrule joints brazed with electroless nickel. Samples were brazed under a variety of conditions and the resultant braze-metal fillets were examined to determine the general quality of the joint as well as the microstructure of the brazing alloy. The structure of a typical tube-to-ferrule fillet of electroless nickel is shown in Fig. 6 (Y-27379). A zone of virtually complete solid solution is present at the center of the fillet where the joint spacing is a minimum. However, several hairline cracks are present in the brittle, eutectic phase at the outer edges of the joint. A portion of this fillet is shown at higher magnification in Fig. 7 (Y-27378). The hairline crack which had propagated through the eutectic structure stopped at the beginning of the region of complete solid solution which can be seen at the left edge of the photomicrograph. Micro-hardness measurements substantiated the expected ductilities of various phases noted in the microstructure. Typical average results, listed as follows:

Eutectic	537 DPH,
Base metal	152 DPH,
Solid-solution zone	234 DPH,

indicate that this solid-solution zone is appreciably softer than the eutectic structure.

In view of the importance of this solid-solution zone as a barrier to crack propagation, several experiments were conducted to ascertain whether or not the width of the zone could be increased by varying the brazing cycle. These results are summarized in Table III. Perusal of these data indicates that within the range of brazing conditions considered, no significant systematic variations in the width of the zone were noted. Rather, the width of this region randomly varied from 0.015 in. to 0.023 in. It is possible that the phosphorous content of the plate plays a more significant role in determining the width of the ductile zone than does the thermal history.

For comparative purposes several Microbraz No. 50 (Ni-Cr-P) joints brazed under similar conditions were also examined and results are tabulated in Table III. Although the actual width of the solid-solution zone in the

Y-27379

Fig. 6. Typical Electroless-Nickel Braze Metal Fillet Joining Type 304 Stainless Steel Fuel Tube to Type 304 Stainless Steel Ferrule Spacer. Zone of complete solid solution can be seen at center of joint. Etchant: 5% CrO_3 , electrolytic.

Y-27378

Fig. 7. Higher Magnification Photomicrograph of Same Fillet as Shown in Fig. 6. Hairline crack seen in brittle, eutectic region does not propagate into the solid-solution zone on left of picture. Etchant: 5% CrO_3 , electrolytic.

TABLE III

MEASUREMENTS OF SOLID-SOLUTION ZONE IN BRAZED TUBE-TO-FERRULE JOINTS

Metallographic Specimen No.	Brazing Alloy	Brazing Temperature (°F)	Brazing Time (min.)	Brazing Atmosphere	Relative Cooling Rate	Width of Ductile Zone (in.)
19525	Electroless Ni	1800	15	H ₂	rapid ^a	0.019, 0.015
19995	Electroless Ni	1800	60	H ₂	rapid ^a	0.019, 0.023
19996	Electroless Ni	1800	60	H ₂	rapid ^a	0.020, 0.017
19841	Electroless Ni	1800	60	H ₂	rapid ^a	0.018, 0.021
20299	Electroless Ni	1850	60	Vacuum	slow ^b	0.020, 0.020
19994	Electroless Ni	1900	15	H ₂	rapid ^a	0.018
19993	Electroless Ni	1900	60	H ₂	rapid ^a	0.018
19842	Electroless Ni	1900	60	H ₂	rapid ^a	0.022, 0.022
18423	Microbraz No. 50	1800	30	H ₂	rapid ^a	0.024 ^c
18424	Microbraz No. 50	1850	30	H ₂	rapid ^a	0.020 ^c
18653	Microbraz No. 50	1850 + rerun	30 + 30	H ₂	rapid ^a	0.020 ^c
19190	Microbraz No. 50	1850	30	Vacuum	slow ^b	0.000, 0.000 ^c
18425	Microbraz No. 50	1900	30	H ₂	rapid ^a	0.018 ^c

^a Pulled into water-cooled zone of furnace immediately after brazing (initial cooling rate approximately 270°F/min).

^b Furnace-cooled from brazing temperature (cooling rate approximately 5°F/min).

^c Measurements corrected for lack of flow at base of joint.

Microbraz No. 50 joint is often wider than the same region in electroless-nickel fillets, the "effective" width is very comparable. This results from the fact that flow of the root of the Microbraz joints was not always complete and a small void was present in some cases. This observation suggests that electroless nickel has slightly superior flow characteristics to Microbraz No. 50. It should also be noted from Table III that one Microbraz No. 50 joint contained no solid-solution zone while this ductile region was present in every joint prepared with electroless nickel. Although these joints appear to be adequate on the basis of metallographic examination, testing of full-size bundles should be conducted in an environment which closely simulates in-pile service conditions, in order to provide assurance that fractures will not propagate through the fillet.

B. Mechanical Testing

A simple test was devised to semi-quantitatively measure the mechanical properties of brazed joints under stress conditions approximating those which would be experienced in a reactor if adjacent fuel tubes expanded longitudinally by different amounts. The specimens used for this test are shown in Fig. 8 (Y-26030) while the specimen assembled in the testing jig is shown in Fig. 9 (Y-26218). Loading was accomplished in a conventional tensile machine with the force applied as indicated. The joints were loaded in a manner which initially approximated pure shear. As the load increased, some deformation of the ferrules occurred and bending moments were introduced producing a more complex stress system. Results obtained in this test on joints brazed with Microbraz No. 50 have been previously discussed.⁸ Results of the strength tests for type 304 stainless steel tube-to-ferrule joints brazed with electroless nickel are summarized in Table IV. Since the stress system is relatively complex, failure strengths are reported in pounds rather than pounds per square inch. Data for Microbraz No. 50 obtained on comparable specimens are also included for comparison purposes. From the data presented, the following conclusions may be drawn:

1. Loads of 1000 - 2100 lb are required to produce failure in reference N. S. Savannah joints brazed with electroless nickel.

2. The considerable spread in the reported data is probably due both to small specimen misalignments which produce increased bending moments and to variations in the size of the brazed fillets.

⁸Maritime Reactor Proj. Ann. Prog. Rep. for Per. End. Nov. 30, 1958, ORNL-2657, pp 24 - 26 (January 23, 1959).

Y-26030

Fig. 8. Specimen for Fuel Tube-To-Ferrule Joint Strength Test.

Fig. 9. Specimen Assembled in Tube-To-Ferrule Joint Strength Test Rig.

TABLE IV

FAILURE STRENGTH OF TUBE-TO-FERRULE^{a,b} JOINTS BRAZED WITH
ELECTROLESS NICKEL AND MICROBRAZ NO. 50

Brazing Temperature (°F)	Brazing Time, min.	Brazing Alloy	No. of Test Specimens	Failure Load	
				Range (lb)	Average (lb)
1800	15	Electroless Ni	3	1000 - 1070	1030
1800	60	Electroless Ni	5	1520 - 2110	1760
1900	15	Electroless Ni	3	1020 - 1510	1220
1900	60	Electroless Ni	5	1010 - 2000	1370
1850	30	Microbraz No. 50	4	1140 - 1460	1330

^a Ferrules - 0.020-in. wall x 1 in. long

^b Tubes and ferrules - Type 304 stainless steel

3. On the basis of limited data, it appears that brazing times of 60 min at either 1800°F or 1900°F produce slightly stronger joints than when brazing for 15 min at the same temperature.

4. On the basis of this type of test the strength of joints brazed with electroless nickel and with Microbraz No. 50 is roughly comparable.

A few tests have been made using the Miller-Peaslee proposed standard braze-joint test specimen.⁹ Details of the testing procedure are illustrated in Fig. 10 (Y-28509). It was somewhat difficult to employ this test with electroless brazed joints since insufficient filleting occurred in several samples. However, three specimens were successfully tested and an average shear strength of 23,800 psi was obtained. This value may be compared with average shear strength of 29,100 psi for three similar specimens of Microbraz No. 50.

One final mechanical test was employed in an attempt to provide a more adequate quantitative measure of the effects of brazing conditions and heat treatment on the quality of the electroless nickel brazed to joints. This was a tension-impact test similar to that suggested by KAPL workers.¹⁰ The test specimens, illustrated in Fig. 11 (Y-28508), were fractured in a conventional impact-testing machine using the tension-impact accessories. The rings in these specimens are machined from 0.080-in.-thick stock. It was observed in the initial experiments with these specimens that large amounts of deformation occurred in the ring indicating that an appreciable portion of the imparted energy was spent in plastic deformation of the specimen rather than shear of the brazed joints. The test was subsequently modified by attaching a 1/4-in.-thick back-up ring to the specimen prior to testing. In this manner, deflections were reduced considerably. The range of impact energies obtained from six specimens was 7.0 - 11.0 ft-lb while the mean value was 9.5 ft-lb. The shear area was 0.126 in.² in each specimen.

V. FUEL ELEMENT FABRICATION AND INSPECTION

To determine whether brazing with electroless nickel could be extended to large components, a fuel bundle similar to that being used by the Maritime Reactors Branch for irradiation tests in the Vallecitos Boiling Water Reactor (VBWR) was brazed. The VBWR test bundle contains sixteen, 40-in.-long type

⁹F. M. Miller and R. L. Peaslee, "Proposed Procedure for Testing Shear Strength of Brazed Joints," Welding J. 37(4), 144s - 150s (1958).

¹⁰Reactor Technology Quar. Rep. No. 4 Metallurgy and Materials, KAPL-2000-1 (January, 1958) pp D89 - D90.

ONE INCH

Fig. 10. Miller-Peaslee Shear-Test Specimens at Various Stages of Processing.

- 25 -

Fig. 11. Brazed-Joint Impact-Test Specimen Before and After Assembly.

304 stainless steel fuel tubes, 0.500-in. dia x 0.035-in. wall in 4 x 4 square array, appropriately spaced by 1-in.-long ferrules.

Ferrules for the sample bundle were plated with approximately 0.7 mils of electroless nickel. The fuel tubes were straightened in a conventional tube straightener and had a maximum initial bow of 0.003 in. Fuel tubes and ferrules then were assembled in the steel brazing jig shown in Fig. 12 (Y-27819). Small fingers which can be seen protruding through the base plate of the jig maintained interrod spacing and positioned the ferrule spacers. After coating all parts of the jig with an alumina-H₂O slurry, the component parts of the jig were assembled into a box and secured with the bolts illustrated in Fig. 12, as well as "C" clamps. After oven drying to remove water from the stop-off, the bundle was placed in the brazing furnace and brazed in H₂ having a dew point of -55°F. The brazing cycle included heating the unit slowly to 1560°F and holding for 30 min to obtain a uniform temperature distribution, heating rapidly to 1850°F and holding for 15 min. The element was then furnace cooled to room temperature. The brazed bundle is shown in Fig. 13 (Y-27820) while a close-up of one end is presented in Fig. 14 (Y-27821). Portions of the small, uniform fillets may be noted.

Visual inspection of the two end planes of spacer ferrules revealed that of the 72 joints visible, all were brazed. This represents one-third of the total joints in the bundle. Joints associated with the interior ferrules were not visible for inspection.

Dimensional measurements of bow, squareness, and interrod spacing were also made. Bow measurements involved determination of the maximum deviation of each bounding plane of four tubes from the horizontal. Measurements are listed as follows:

Top side	-5 mils
Right side	+3 mils
Bottom side	+17 mils
Left side	-18 mils

Squareness measurements were taken on the four corners at each end of the bundle with a machinist's protractor. These determinations represented the deviation of two adjacent planes of tubes from a right angle. The maximum and average deviations were 1.0 deg and 0.28 deg, respectively.

Y-27819

Fig. 12. Brazing Jig With Partially Assembled VBWR-Type Test Fuel Element.

Fig. 13. VWR-Type Test Fuel Bundle Brazed with Electroless Nickel.

Fig. 14. Close-up of One End of Fuel Bundle Shown in Fig. 13.

Interrod spacing was measured adjacent to and midway between ferrules in each segment of the bundle by inserting drill rods of known diameters between the fuel tubes. The average interrod spacing from top to bottom was 0.117 ± 0.005 in. and the average spacing from right to left was 0.107 ± 0.005 in. -0.009 -0.004 . This small difference was undoubtedly caused by uneven clamping pressure on the brazing jig.

VI. CORROSION STUDIES

On the basis of corrosion tests on nickel-phosphorous alloys conducted at ORNL and other sites, it was anticipated that these materials would exhibit excellent resistance to attack by high-temperature water. In the ORNL tests,¹¹ T-joints of type 304L stainless steel brazed with a 10 wt % P-Ni alloy were exposed in static distilled water at 1200 psi and 565°F for 1000 hr. The specimens exhibited a weight loss of 0.12 mg/cm^2 and contained pits $1/2$ mil in depth. Tests conducted in conjunction with the Yankee Reactor Program¹² indicated that electroless nickel had corrosion resistance equivalent to type 304 stainless steel and Nicrobraz No. 50.

To verify these results, a few additional tests are in progress with three types of samples being evaluated. One is a tube-to-ferrule fillet, the second is a section of a three-ply sandwich, and the third is a 0.015-in.-thick square of stainless steel with a deposit of electroless nickel on one surface. This third specimen was prepared by depositing an electroless-nickel plate about 0.7 mils thick on the stainless steel sheet and brazing the sample in H_2 at 1800°F for 15 min. All specimens were manufactured from type 304 stainless steel. After 300 hr of static autoclave testing at 525°F, neither of the first two specimens exhibited any visual evidence of distress in terms of bond-line attack, pitting, or crevice effects. The third specimen had a weight loss of 0.1 mg/cm^2 which is equivalent to a penetration of 0.1 mil/year. These tests are continuing.

VII. CONCLUSIONS

1. Electroless nickel appears to be suitable as a brazing alloy for assembling fuel bundles of the type specified for the N. S. Savannah.

¹¹R. J. Beaver, Metallurgy Division Semiann. Prog. Rep. for Per. End. Oct. 10, 1954, ORNL-1875, p 82 (August 12, 1955) (SECRET).

¹²R. W. Garbe and H. E. Walchli, Quar. Prog. Rep. for Per. July 1 to Sept. 30, 1958, YAEC-97, p 29 (November 14, 1958) Unclassified.

2. Plating of spacer ferrules with electroless nickel measurably reduces the time required for fuel element assembly.

3. Electroless-nickel-brazed tube-to-ferrule joints are characterized by a brittle, eutectic phase of the outer edges at the fillet and a ductile solid-solution zone near the center of the fillet. Although cracks readily form in the brittle area, they do not appear to propagate through the ductile zone. This conclusion should be substantiated by engineering tests on full-size bundles under appropriate conditions of stress, vibration, and thermal gradient.

4. The shear strengths of electroless-nickel joints and Microbraz No. 50 joints are 23,800 psi and 29,100 psi, respectively.

5. No significant differences were observed in joints brazed at 1750, 1800, 1850, and 1900°F for periods of 15 to 60 min, and post-brazing heat treatments at 1560°F for various times did not discernibly alter the microstructure.

5. Joints brazed with electroless nickel exhibited no appreciable attack after 300 hr in 525°F static water.

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