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WELDABILITY OF ELECTROFORMED NICKEL

L. D. Frye

March 1979

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OAK RIDGE, TENNESSEE**

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WELDABILITY OF ELECTROFORMED NICKEL

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ABSTRACT

An investigation was conducted to identify the cause of variations in the weldability of electroformed nickel. Evaluation of gas tungsten-arc welds in 0.254-mm-thick electroformed nickel sheet by chemical analyses of the nickel base material identified phosphorus and sulfur contamination as the cause for welding variability. A screening test was developed that predicted the weldability of electroformed nickel.

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SUMMARY

Phosphorus and sulfur have been identified as two elements that cause welding variability in electroformed nickel. A screening test consisting of a 30-minute anneal at 1000° C followed by metallographic evaluation was developed to predict weldability. A welding procedure was developed that produced sound welds consistently in 0.254-mm-thick electroformed nickel cylinders.

INTRODUCTION

Electroforming has been utilized at the Oak Ridge Y-12 Plant^(a) to make close-tolerance sheet metal containers. This process, which electrodeposits nickel onto a precisely machined mandrel, produces parts that are identical to the contour of the mandrel. The method has unique advantages for fabricating single parts since the only prerequisite is the machining of the mandrel. The fact that this mandrel can be used many times makes this also a useful process for producing multiple parts. Because of these advantages, electroforming of nickel was selected as the process for making 0.254-mm-thick, circumferentially welded, cylindrical shapes.

Sample material was obtained from Sandia - Livermore for the purpose of preparing a welding procedure. All the material was cleaned and welded by using similar parameters. During the welding, porosity was evident in welds on some of the electroformed nickel plates, but not on others. The purpose of this investigation was, therefore, to find out why some plates produced good, sound welds and other plates produced porous welds.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

WELDABILITY OF ELECTROFORMED NICKEL

BACKGROUND LITERATURE

The literature reports many possible causes for the porosity problem. Improper cleaning or handling of the material may produce porosity when welding.¹ Shielding gases must be pure. Any oxygen, carbon dioxide, or nitrogen additions will cause porosity. Excessive amounts of these same gases in the base metal will also cause porosity when welding.² Welding parameters such as welding speed also affect the soundness of the finished weld, especially when no filler metal is added.³ A given thickness of material has an optimum welding speed range for minimum porosity. Travel speeds outside that range, either too fast or too slow, mean increased porosity.¹

Certain minor elements present in a nickel structure can also be the cause of porosity problems. Pease¹ has shown that sulfur is the most subversive element to the welding of electroformed nickel. Sulfur causes embrittlement of the weld metal and heat-affected zone (HAZ). This embrittlement is generally associated with cracking; but, residual stresses, which produce and propagate cracks, are minimal when welding thin material. The dominating factor when welding thin material is the large size of the HAZ. If embrittlement of the HAZ is present, a larger HAZ will have more gas diffusing into the weld metal which will account for the large amounts of porosity in the weld metal of thin material. Pease¹ also reported that lead and phosphorus cause embrittlement much like sulfur, and that as little as 20 ppm phosphorus can have damaging effects on wrought nickel.

Dini, Johnson, and Saxton⁴ have reported that nickel deposits containing more than 50 ppm sulfur could not be used in high-temperature applications which include welding. Phase diagrams of nickel/sulfur and nickel/phosphorus are included in this report (Figures A-1 and A-2, Appendix).

EXPERIMENTAL WORK

The great difference in the weldability of electroformed nickel sheets can be seen by comparing Figures 1 and 2. The following experimental work had two general objectives: (1) to find alternate or corrective welding procedures, and (2) to find chemical differences between weldable and nonweldable material.

Alternate methods of joining, and corrective measures in the welding procedure that might stop or minimize the porosity include: (1) an alternate cleaning procedure, (2) an alternate shielding gas coverage, (3) gas tungsten-arc (GTA) brazing, and (4) electron-beam (EB) welding.

Analytical methods used to determine the cause of the porosity problem include: (1) chemical analysis of each nickel plate, (2) metallographic examination of heat-treated samples and cross-sectional views of bead-on-plate welds, (3) thermogravimetric analysis (TGA), (4) electron microprobe analysis of the base metal, the HAZ, and weld metal, and

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Figure 1. GAS TUNGSTEN-ARC WELD BEAD ON 0.254-mm-THICK ELECTROFORMED NICKEL. (Shown is the Gross Porosity that was Encountered when Welding some Plates; As Polished; 75X)

(5) scanning electron microscopy (SEM) of fractured surfaces consisting of portions of the base metal, the HAZ, and the weld metal.

A test to confirm good-quality material from different electroplating baths was developed; and, to conclude the investigation, nickel was plated, tested, and welded.

EXAMINING ALTERNATE CLEANING AND WELDING PROCEDURES

To begin the investigation, cleaning and welding parameters were evaluated to make sure the porosity was not caused by the welding procedure. Special care was used to ensure that both the weldable and unweldable material were treated exactly the same. Various cleaning methods were used to remove any tenacious sulfur films that might be present due to shipping, handling, or storing of the electroformed nickel. Both mechanical cleaning (using a wire brush and an alcohol rinse) and chemical cleaning were used. Chemical cleaning involves soaking the part in a detergent, rinsing, pickling for three minutes in hydrochloric acid (30 vol %), rinsing, and air drying. Both cleaning operations provided good results for the weldable material, but did not help the welding problem on the unweldable material.

Since shielding gases can have an effect on porosity, several different gases were tried. The best shielding gas found was a mixture of argon and hydrogen (95% Ar and 5% H₂). The added hydrogen gave a deoxidizing effect to the arc which helped reduce porosity.

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Figure 2. GAS TUNGSTEN-ARC WELD BEAD ON 0.254-mm-THICK ELECTROFORMED NICKEL. (A Sound Weld with No Porosity; As Polished; 75X)

Hydrogen also produced a hotter arc; therefore, the gases present in the weld metal were given more time to diffuse to the surface before solidification took place.

Braze welding was explored as a possible solution to the porosity problem. A lap joint was used with a 0.127-mm-thick brazing alloy shim (72% Ag and 28% Cu) placed between the nickel parts. A GTA torch was passed along the joint to supply the heat. The joint was found to be leak tight when checked with dye penetrant. Metallography indicated that very little melting of the nickel took place and then only on the edge of the top sheet. The bottom sheet was heated above the recrystallization point, and adequate heat was present for the braze material to flow and wet both nickel surfaces. Although this method appeared to be satisfactory, it was not examined further because additional material in the joint was not desirable.

Next, EB welds were made on the material that had produced porosity when using GTA welding. Both a lap joint and a bead-on-plate joint were welded. No leaks were detected while using the dye penetrant; however, a study that used metallography disclosed micro-porosity in the grain boundaries of the HAZ. This embrittlement of the HAZ meant that any type of fusion weld would not be desirable when joining the unweldable nickel.

Several samples of the unweldable material were heated to different temperatures and then examined for embrittlement. It was found that embrittlement of the electroformed nickel

began to occur in the range of 600^o C. As mentioned previously, 50 ppm sulfur present in the electroformed nickel would cause problems at high temperatures, but preliminary chemical analysis by spark source mass spectrography indicated that the unweldable nickel plates contained less than 50 ppm. This result would mean that sulfur contents of less than 50 ppm do affect the weldability of the electroformed nickel; or, possibly, other elements such as phosphorus, lead, or combinations of these elements were embrittling the nickel.

The absence of visible porosity in the EB samples of the unweldable material was attributed to the fast freezing rate and small HAZ associated with the EB weld. These two factors prohibited the gases from forming larger bubbles before the weld metal solidified. This effect can be seen in Figure 3.

Since HAZ embrittlement was found in the EB weld, each of the previous welds were examined again. Heat-affected-zone embrittlement in all the welds would mean that minor elements were the cause of the porosity problem. All of the welds in the "nonweldable" material did have HAZ embrittlement; therefore, the remainder of the investigation looked for chemical differences between the weldable and nonweldable material.

Gas tungsten-arc welding was used to complete the investigation instead of EB welding because it had better fixturing capabilities, less fit-up problems, and provided easier joint tracking. The GTA welding technique also gave the gas bubbles a longer time to coalesce (see Figure 4) which resulted in larger pores in the solidified weld metal.

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Figure 3. ELECTRON-BEAM WELD IN ELECTROFORMED NICKEL. (HAZ Embrittlement and Weld-Metal Porosity; Note Weld Metal Porosity has not Diffused into the Larger Voids; Polished and Etched; 750X)

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Figure 4. GAS TUNGSTEN-ARC WELD BEAD ON 0.254-mm-THICK ELECTROFORMED NICKEL. (HAZ with Grain-Boundary Porosity Plus Weld-Metal Porosity; Polished and Etched; 750X)

ANALYTICAL ANALYSIS OF ELECTROFORMED NICKEL

Thermogravimetric analysis (TGA) was performed on the nickel part at a constant heating rate of $8^{\circ}\text{C}/\text{min}$ and in a vacuum of 0.4 mPa ($3 \times 10^{-6}\text{ torr}$). The gases given off during this process were monitored by a quadrupole mass spectrometer. Figure 5 shows that sulfur dioxide and nitrogen monoxide were given off by the nonweldable material and not the weldable material. Primary concern was with sulfur because of the uncertainty of nitrogen gas coming off the weldable sample, and also sulfur forms a very-low-melting eutectic with nickel.

Electron microprobe analysis of both weldable and nonweldable electroformed nickel is listed in Table 1. Phosphorus was monitored because of its low eutectic with nickel and its similarity to sulfur in its detrimental influence on nickel. The electron microprobe's detection limit for sulfur and phosphorus was less than 20 ppm which value was determined by comparing counts from the electroformed nickel to a nickel standard, an indium phosphide standard, and an iron sulfide standard. A bead-on-plate weld was made on both the weldable and nonweldable material. These samples were then examined in three major areas—the base metal, the HAZ, and the weld metal. Neither sulfur nor phosphorus was detected in any of these areas in the weldable sample; in the nonweldable material, phosphorus and sulfur were detected in the base metal and in the HAZ.

Figure 5. THERMOGRAVIMETRIC ANALYSIS PERFORMED ON ELECTROFORMED NICKEL. (Note Expulsion of SO₂ from the Nonweldable Material)

Table 1

ION-MICROPROBE ANALYSIS OF ELECTROFORMED NICKEL

Location	Impurity Content (ppm)	
	Phosphorus	Sulfur
<u>Good Specimen (weldable)</u>		
Outside the HAZ	None Detected (< 20)	None Detected (< 20)
Inside the HAZ	None Detected (< 20)	None Detected (< 20)
Inside the Weld Zone	None Detected (< 20)	None Detected (< 20)
<u>Bad Specimen (nonweldable)</u>		
Outside the HAZ	25	24
Pits Outside the HAZ (not many present)	73	81
Grains Inside the HAZ	34	20
Pits in the Grain Boundaries Inside the HAZ	347	123
Weld Zone	None Detected	None Detected

The scanning electron microscope (SEM) was used in an attempt to verify the findings of the electron microprobe; however, this verification could not be accomplished because the

SEM could not detect the low amounts of phosphorus and sulfur. But the SEM did give good high-magnification photographs of the porosity of the HAZ grain boundaries which did verify HAZ embrittlement.

ANNEALING TEST

Since the weldability of electroformed nickel was dependent upon its composition, annealing was used to test the material's weldability and also test its chemical composition.^{4,5}

The annealing test consisted of heating a coupon that was plated with a part to 1000°C for 30 minutes, then metallography was used to examine the coupon for grain-boundary degradation. If the grains recrystallized with no porosity along the grain boundaries, the part was chemically sound and weldable; but, if the coupon recrystallized with porosity along the grain boundaries, the part was not weldable, heat treatable, or chemically sound. Examples of each can be seen in Figures 6 and 7. This test can be used by electroplaters to test their bath's chemical composition and cleanliness^{6,7} and also by welders to certify the product's weldability.

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Figure 6. ELECTROFORMED NICKEL THAT WAS ANNEALED AT 1000°C FOR 30 MINUTES. (This Material will Produce No Porosity when Welded; Polished and Etched; 750X)

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Figure 7. ELECTROFORMED NICKEL THAT WAS ANNEALED AT 1000° C FOR 30 MINUTES. (This Material will Produce Porosity when Welded; Polished and Etched; 750X)

WELDING PROCEDURE

To conclude the investigation, a welding procedure was formulated and evaluated for making a leak-tight circumferential weld in 0.254-mm-thick electroformed nickel. The procedure is outlined in Table A-1 of the Appendix. Successful leak-tight, circumferential welds were made by using this procedure.

REFERENCES

1. Pease, G. R.; "The Practical Welding Metallurgy of Nickel and High Nickel Alloys", *Welding Journal*, **36**, (7), Research Supplement, pp 330S - 334S; July 1957.
2. Conaway, H. R.; "Welding the Nickel Alloys, Part 3: GTAW, SAW, and OAW", *Welding Design and Fabrication*, pp 106 - 110; April 1977.
3. Hinde, J. and Thorneycroft, D. R.; "Welding of Nickel and High-Nickel Alloys by Inert Gas Shielded-Arc Processes", *British Welding Journal*, pp 411 - 419; October 1955.
4. Dini, J. W., Johnson, H. R., and Saxton, H. J.; "Influence of Sulfur on the Properties of Electrodeposited Nickel", *J Vacuum Science Technology*, **12**, (4), pp 766 - 769; July/August 1975.
5. Carlin, F. X.; "Prevention of Poor Adhesion Between Lamellae in Thick Nickel Deposits and Electroforms", *Plating*, **55**, pp 148 - 151; February 13, 1968.
6. Schuler, F., Rocketdyne; *Personal Communications*.
7. Waldrop, R. C., Union Carbide Corporation-Nuclear Division, Y-12 Plant; *Personal Communications*.

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APPENDIX

PHASE DIAGRAMS AND PROCEDURAL DATA

Figure A-1. NICKEL/SULFUR PHASE DIAGRAM. (Note the Low Eutectic at 645° C)

Table A-1

WELDING PARAMETERS FOR MAKING A
CIRCUMFERENTIAL WELD IN 0.254-mm
THICK ELECTROFORMED NICKEL

Process	Gas Tungsten-Arc Weld
Shielding Gas	Argon/5% Hydrogen
Shielding Cup (mm)	9.52 x 39.69
Electrode Size (mm)	1.59
Electrode Type	2% Thoriated Tungsten
Current Type	DSCP
Current (A)	15
Arc Distance (mm)	0.508
Travel Speed (mm/min)	254
Joint Design	Lap Joint
Cleaning Method	Wire Brush - Alcohol Rinse

Figure A-2. NICKEL/PHOSPHORUS PHASE DIAGRAM. (Note the Low Eutectic at 880°C)

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