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FINAL REPORT
TO
LOS ALAMOS NATIONAL LABORATORY
FOR
PROTOTYPE NICKEL COMPONENT DEMONSTRATION

by

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PROTOTYPE NICKEL COMPONENT DEMONSTRATION

SUMMARY

For the past two years, BIRL, Northwestern University's industrial research laboratory, has been developing a process to produce high-purity nickel structures from nickel carbonyl using chemical vapor deposition (CVD). The prototype demonstration effort had been separated into a number of independent tasks to allow Los Alamos National Laboratory (LANL) the greatest flexibility in tailoring the project to their needs. LANL selected three of the proposed tasks to be performed: Task 1 - System Modification and Demonstration, Task 2 - Stainless Steel Mandrel Trials, and Task 4 - Manufacturing Study. Task 1 focused on converting the CVD system from a hot-wall to a cold-wall configuration and demonstrating the improved efficiency of the reactor type by depositing a 0.01-inch-thick nickel coating on a cylindrical substrate. Since stainless steel substrates were preferred because of their low α -emitter levels, Task 2 evaluated mandrel configurations which would allow removal of the nickel tube from the substrate. The manufacturing study was performed to develop strategies and system designs for manufacturing large quantities of the components needed for the Sudbury Neutrino Observatory (SNO) program. Each of these tasks was successfully completed. During these efforts, BIRL successfully produced short lengths of 2-inch-diameter tubing and 6-inch-wide foil with levels of α -radiation emitting contaminants lower than either conventional nickel alloys or electroplated materials. We have produced both the tubing and foil using hot-substrate, cold-wall reactors and clearly demonstrated the advantages of higher precursor efficiency and deposition rate associated with this configuration. We also demonstrated a novel mandrel design which allowed easy removal of the nickel tubing and should dramatically simplify the production of 1.5-meter-long tubes in the production phase of the program. With this background, and our previous experience with process scale-up, we have the demonstrated expertise to fabricate prototype components and transition to production of these items for the SNO Program.

INTRODUCTION

The success of the Sudbury Neutrino Observatory will depend on the production of detectors made from nickel with extraordinarily low levels of α -radiation

emitting contaminants, such as uranium, thorium, and cobalt. In conventional nickel products, the level of these materials is vastly greater than the 10 parts-per-trillion (ppt) by weight needed in the detectors. Researchers at LANL contracted with BIRL to produce nickel by chemical vapor deposition (CVD) using nickel carbonyl as a precursor. This processing route includes several *defacto* purification steps, such as multiple condensations and evaporations. These purification steps, coupled with the fact that the α -emitters, generally, do not form carbonyls, allow for a high-purity nickel to be produced using this process route.

Nickel carbonyl, $\text{Ni}(\text{CO})_4$, is used commercially to produce nickel powders and, by a few small companies, to apply coatings to dies and molds. The carbonyl can be used to deposit nickel from room temperature to approximately 300°C, it has a vapor pressure of approximately 360 torr at room temperature, and it is non-reactive with many materials. However, nickel carbonyl is extremely toxic (TLV 0.1 ppm), and this has greatly limited its use for deposition processes. In order to work safely with nickel carbonyl, very specific facility and procedural modifications must be adopted to insure complete containment and neutralization of the carbonyl. BIRL had previously made these modifications to one of our hot-wall CVD reactors for a previous client, and LANL was able to take advantage of these existing facilities for a demonstration program.

The experiments we performed for LANL in the hot-wall reactor demonstrated the deposition of high-purity nickel and allowed an initial screening of candidate substrate materials. Typical deposition conditions for these runs were a reactor temperature of 200°C at a pressure of approximately 200 torr. The substrates were selected in conjunction with LANL for their very low level of α -emitting contaminants and a coefficient of thermal expansion (CTE) higher than nickel. The first two candidates evaluated were 304 stainless steel (SS) and Teflon™. Substrates for both the tube and sheet were fabricated from each material. The concept was to use substrates with a higher CTE than nickel so that upon cooling from the deposition temperature, or upon further cooling with liquid nitrogen, the nickel coating would pull away from the substrates. The tube mandrels were approximately 2 inches in diameter and 18 inches long while the substrates for the sheets were 4 inches wide and 18

inches long. The surface finish of the 304 SS tube mandrels was as-machined, but we did evaluate a phenolic resin coating to provide a smoother deposition surface.

The first several deposition tests were to develop parameters which produced smooth and ductile nickel on the substrates while achieving a reasonable coating rate. If nickel carbonyl is thermally decomposed at higher pressures (above a few torr), the carbon monoxide can disproportionate in the reaction shown in equation 1.



If this reaction takes place, the carbon co-deposits with the nickel and produces a brittle and hard coating. In previous efforts by other researchers (1-3), a variety of oxidants have been used to suppress this reaction, including oxygen, nitrous oxide, and water vapor. For this effort, we elected to use carbon dioxide since it would suppress the disproportionation reaction and not just oxidize the carbon that did form. Using carbon dioxide proved to be very effective, and apparently clean coatings were produced directly.

Our initial deposition tests using the hot-wall reactor to form tubes and sheets required between 8 and 12 hours of deposition to build the coating thickness up to the desired 0.01 inch. The coating thickness on the substrates varied both with radial and axial location in the reactor. All of the substrates were coated with nickel, but it was very difficult to release the coating from any of the samples. The adherence of the nickel coating on the as-machined and resin-coated 304 SS mandrels was very high, and the coating could only be removed by using a razor blade to scrape it off in short lengths. Only small amounts of nickel could be removed from the flat 304 SS sheet substrates. The Teflon™ substrates did show evidence of localized nickel debonding, but the net effect was a "wrinkled" or buckled coating. The wrinkled texture was produced by localized areas of debonding and adhesion. "Islands" of the nickel coating would release from the Teflon but were constrained by a network of adherent regions. Thus, as the mandrel shrank, the coating deformed between the adherent regions to take up the strain. The nickel could only be peeled off by hand in small irregular pieces.

One result of these early tests was to demonstrate that the hot-wall reactor configuration was not economic for the production of nickel tubes and other shapes. Deposition efficiencies for the hot-wall system were below 5 percent, which would make production of hundreds of meters of tubing far more expensive. The low efficiency of the hot-wall reactor, and the difficulty removing the nickel from the mandrels, demonstrated that these two issues needed to be addressed before trying to scale up the process.

RESULTS AND DISCUSSION

Task 1 - System Modification and Demonstration

A cold-wall reactor with an inner diameter of approximately 3 inches and a length of 12 inches was inserted in place of the 15-inch-diameter hot-wall reactor (Figure 1). The processing system includes double containment for the carbonyl source, mass-flow monitoring for the carbonyl, mass-flow control for the other reactants, and a neutralization system consisting of a thermal "cracker" and a modified scrubbing system to react any excess nickel carbonyl exiting the reactor. The system controls are located outside of the walk-in hood for remote operation. The substrate consisted of a 304 stainless steel bar machined to a 2-inch diameter and drilled and tapped on one end to accept a $\frac{1}{2}$ -13 bolt. The upper lid of the reactor had a $\frac{1}{2}$ -13 bolt welded to locate the mandrel in the reactor. Unfortunately, the bolt was not perpendicular to the reactor lid, which put the mandrel at a slight angle to the gas flow. The mandrel was heated to the deposition temperature of 200°C using a 1-kilowatt induction heating unit. The angle of the mandrel to the gas flow and to the induction coil caused enough variation in precursor flow and temperature that the coating thickness varied around the mandrel circumference.

The deposition conditions demonstrated in the cold-wall system were very similar to those used in the hot-wall unit, except that the nickel carbonyl flow was reduced to approximately 2 grams per minute. The reactor pressure was held at approximately 200 torr, and carbon dioxide was added to the reactant stream to suppress carbon formation. We performed an experiment to demonstrate the reactor using a lathe-turned mandrel. As we introduced the nickel carbonyl into the reactor, we were able to see the nickel nucleate and grow on the mandrel.

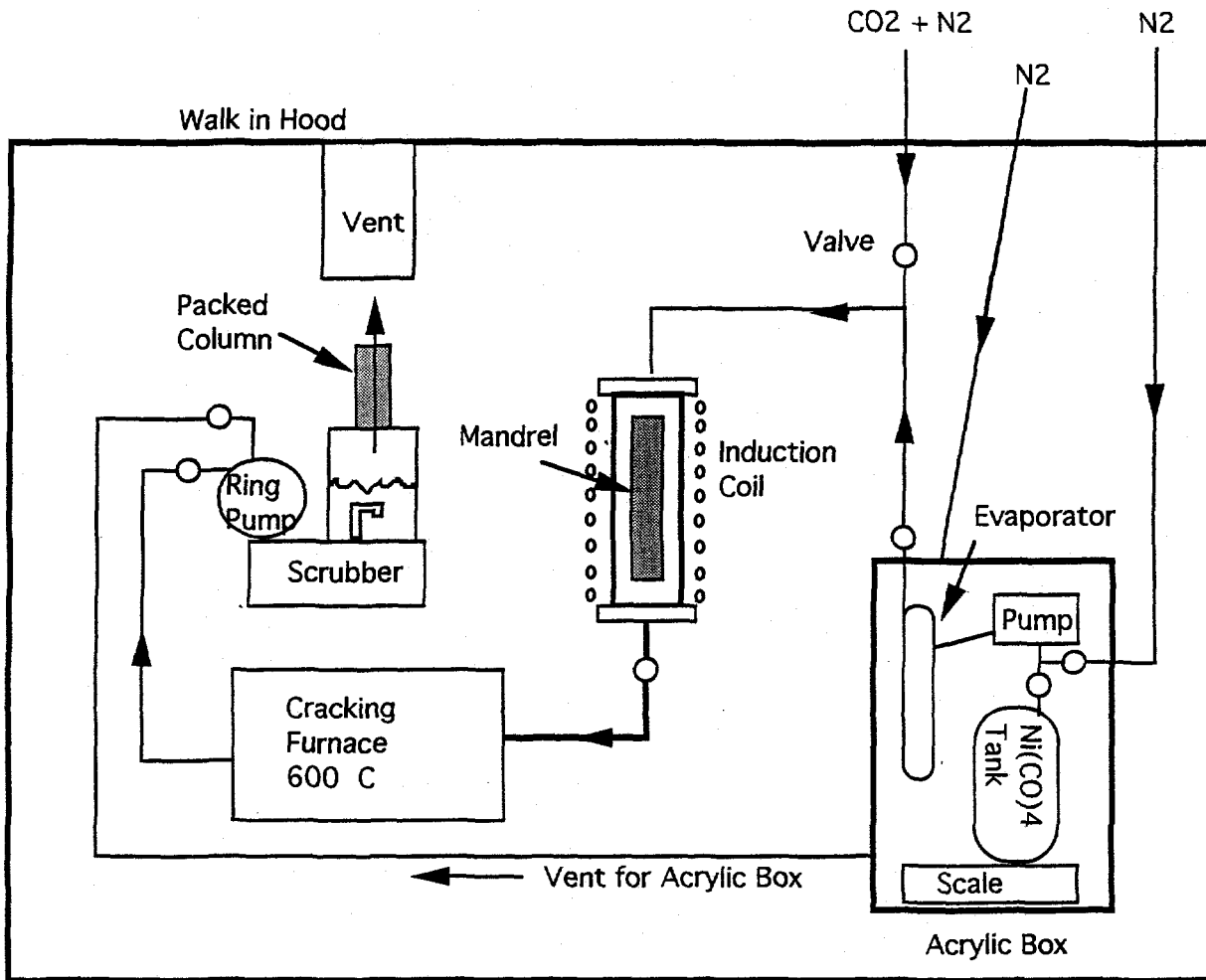


Figure 1. CVD Nickel System Schematic

We ran the system for two hours. The coating on the upper end of the mandrel was 0.012-inch-thick while the bottom coating varied from 0.003 inch to 0.005 inch thick. By measuring the weight gain of the mandrel, we were able to determine that the cold-wall configuration produced a precursor efficiency of almost 40 percent. The cold-wall system produced an 8-fold improvement in precursor efficiency over the hot-wall system and decreased the deposition time to produce a 0.01-inch-thick coating from between 8 and 12 hours to approximately 2 hours. The coating did vary in thickness both radially and axially. The radial variation was predominantly an effect of the mandrel being off-axis to the reactor as mentioned previously. The axial variation was likely caused by too high a deposition efficiency which may have depleted the gas stream. The deposition of the 0.01-inch-thick coating completed this task.

Task 2 - Stainless Steel Mandrel

Demonstrating a technique, or mandrel material, that allowed easy removal of the nickel from the substrate was a critical factor in the demonstration of the CVD fabrication technique. In our hot-wall reactor feasibility study, discussed previously, we had examined a number of mandrel materials during our efforts to produce nickel components, but none of them proved satisfactory. For this task, we fabricated a polished 304 SS mandrel for evaluation. The polished surface of the mandrel would lessen the mechanical interlocking of the coating and mandrel and hopefully allow the nickel to pull way from the substrate due to the CTE mismatch when it was cooled in liquid nitrogen.

While the polished mandrel was being fabricated, we continued development of the deposition parameters for the tubes using the lathe-turned mandrel. By adjusting the total gas flow and the gas-introduction sequence, we quickly developed parameters to produced moderately uniform coatings. The tube produced with these parameters is shown in Figure 2. The tube was produced in 2 hours and was removed from the mandrel by immersing it in liquid nitrogen and then pushing the nickel tube off of the mandrel with a lab press. The tube shown in Figure 2 has an inner diameter of 2 inches and it is 8 inches long. The upper wall thickness varies from 0.008 inch to 0.01 inch, while the lower section has a wall thickness between 0.005 inch and 0.007 inch. This thickness variation was partly due to the mandrel being off-axis in the reactor. The tube has a bright finish on the internal surface and a smooth matte grey external surface. This tube was delivered to LANL for characterization.

When the polished 304 SS mandrel was completed, we used the coating conditions which produced the 8-inch-long tube to evaluate the effect of its less than 10 micro-inch surface finish. At this time, we also reworked the ½-13 bolt on the reactor lid to make it perpendicular to the lid. The first deposition trial we made with this mandrel showed mixed results because the coating uniformity was poor. The coating on the top end of the mandrel was being approximately 0.01 inches thick while the coating at the bottom was only 0.002 inch. When the coated-mandrel was cooled in liquid nitrogen, a gap was visible between the 0.01-inch-thick coating and the mandrel which ran

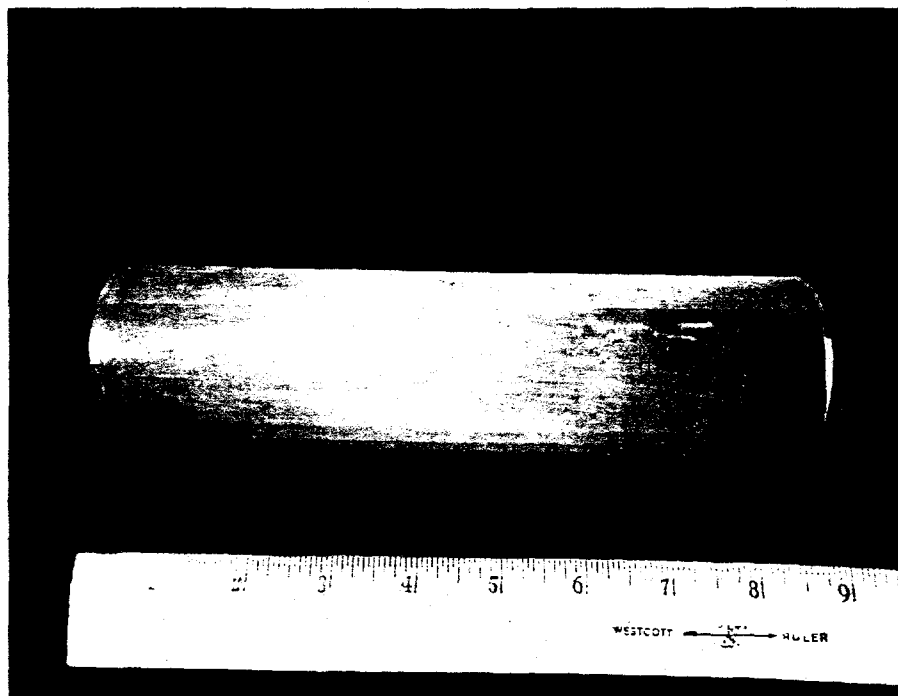
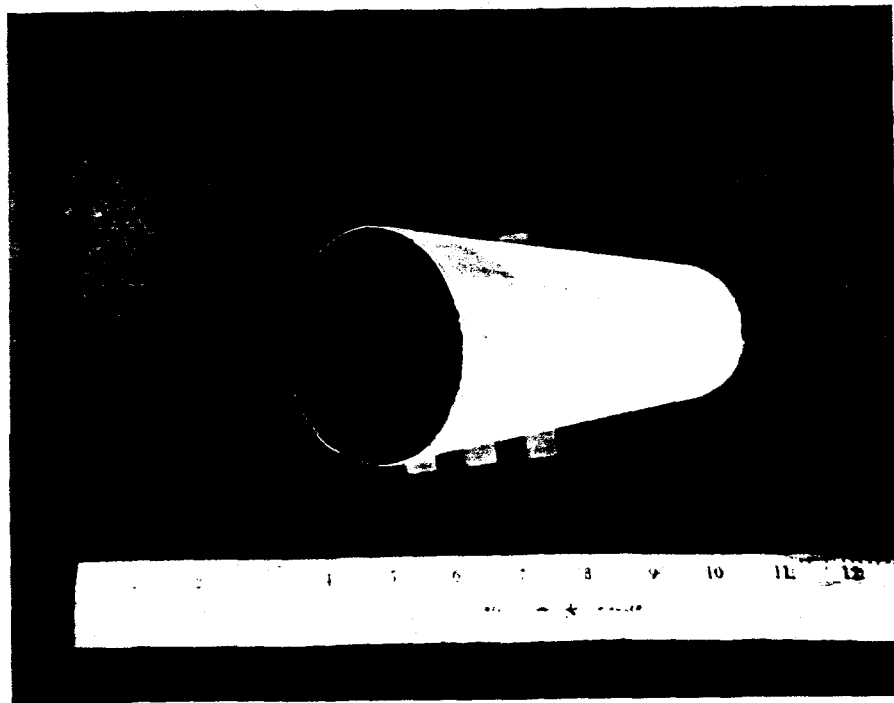


Figure 2. CVD Nickel Tube

along approximately 60 percent of the mandrel circumference. Since we did not want to damage the polished surface of the mandrel, the nickel coating was removed by slitting the coating and peeling it off. The coating did peel off the mandrel very easily, however, which indicated that the polished surface did dramatically reduce mechanical interlocking of the coating and mandrel. We believe that the coating thickness variation greatly contributed to the coating not separating from the substrate and that highly polished substrates may be useful in producing several of the components needed by the SNO Program. The coating from this experiment was later flattened and sent to LANL for examination.

With all of the mandrels tested, the adhesion (mechanical and surface energy) between the coating and the mandrel is great enough that the nickel shrinkage is dominated by the behavior of the thicker mandrel. The stress generated in a coating by a difference in CTE with the substrate is given by equation 2.

$$\sigma_c = \Delta\alpha\Delta T E_c / (1-\nu_c) \quad (2)$$

where, σ_c is the stress in the coating, $\Delta\alpha$ is the difference between the CTE of the substrate and the coating, E_c is the Young's Modulus of the coating, ΔT is the difference between removal and deposition temperatures, and ν_c is the Poisson's ratio of the coating. This equation assumes the coating is thin in comparison to the substrate. Using the following information, $\alpha_{Ni} = 13$ parts-per-million- $^{\circ}K$ (ppm- $^{\circ}K$), $\alpha_{304} = 17$ ppm- $^{\circ}K$, $\Delta T = -200$, $E_c = 199.5$ GPa, and $\nu_{Ni} = 0.312$, the stress in the nickel coating is approximately -232 MPa (-33.7 ksi) and it is compressive. This residual stress is apparently not sufficient to overcome the work of adhesion at the coating-substrate interface except for thick coatings on a very smooth mandrel.

During this project, we conceived of a novel release technique which takes advantage of this thickness-dominated shrinkage behavior. The concept was to use 0.001-inch-thick 304 SS foil as an overlay to the mandrel. We spiral wrapped the foil around the mandrel and trimmed each end of the foil to match the mandrel. Only one clamp was required to secure the foil to the mandrel because the stiffness of the foil and the friction between the foil and mandrel combine to produce a self-locking effect at the other end of the wrap.

By using this very thin foil, ten times thinner than the desired nickel coating, the nickel shrinkage rate would no longer be dominated by the mandrel. If we repeat the CTE-induced stress calculation as before, except that we assume a 0.001-inch "coating" of 304 SS on the inside of a 0.01-inch-thick nickel tube and convert the resulting 232 MPa (33.7 ksi) stress in the 304 SS into strain, we see that the 304 SS is strained 0.11 percent. Since the 0.001-inch 304 SS is wrapped onto a 2-inch-diameter mandrel, this results in a diametrical gap of 0.002-inches. When we tested this concept, the nickel-coated 304 SS foil was free of the 304 SS mandrel when it was cooled to room temperature and it easily slid off the mandrel. Since the foil has a high surface finish as a result of the rolling process, we were able to peel it off the interior of the sample. Unfortunately, the nickel coating on this experiment did not have a uniform thickness along its length and the section with a wall thickness of approximately 0.002 inch tore while removing the SS foil. The nickel coating was delivered to LANL for examination. This technique does leave a spiral step the thickness of the foil along the interior of the tube. If this foil overlay is used in future efforts, we believe that a substantial reduction in mandrel costs can be realized in the production phase, but this must, of course, be verified for the longer tubes and more complex shapes. If the foil wrap technique works for 1.5-meter-long tubes and the other components, the need for either collapsible or highly polished mandrels would be eliminated at a substantial cost savings.

Task 4 - Manufacturing Study

Before producing the large number of full-size components needed by the SNO Program, several technical challenges associated with manufacturing parts using the CVD nickel process must be addressed, including quality control of the nickel carbonyl, the design of efficient production reactors, and the development of fixturing techniques for the parts. Each of these issues will be discussed in separate sections.

Quality Control for Nickel Carbonyl

A major concern with providing a fixed-price quotation for production of the nickel parts for the SNO Program is the potential variability in impurity levels in the nickel carbonyl and other precursors. LANL has analyzed a

variety of nickel samples produced by different processing techniques using radiochemical neutron activation analysis (RNAA). The RNAA was performed on two samples produced by BIRL using CVD from nickel carbonyl, a commercially available Ni 200 alloy, and an electroformed material with the results of the analysis shown in Table 1. The level of uranium and thorium varied by factors of approximately 3 and 7, respectively, within our CVD nickel samples. The only apparent difference between these processing runs was that the nickel carbonyl was supplied by different companies; Noah Technologies and Pressure Chemical, respectively. We have been able to identify only three producers of nickel carbonyl: Inco, Mirotech (Ontario, Canada), and FET Engineering (Kentucky). Pressure Chemical has ceased production of nickel carbonyl and has a remaining stock of approximately 1,200 pounds. Noah Technologies has also ceased production. Noah Technologies nickel carbonyl was used to produce the 4/93 sample, while Pressure Chemical material was used to for the 12/93 sample. Inco, Mirotech, and FET Engineering generate the carbonyl on-site for their internal use and do not sell it.

Table 1. RNAA Results on Various Nickel Samples

Sample	U(ppt)	Th(ppt)
BIRL Flakes (4/93)	17.0 ± 2	57 ± 3
BIRL Tube (12/93)	5.2 ± 9	393 ± 16
Ni 200 Sheet	26,600 ± 1,000	344 ± 21
Electroformed (12/93)	≤ 139	≤ 20

The results from the RNAA indicate that variations in nickel carbonyl purity at least from supplier-to-supplier, and possibly from lot-to-lot, are a significant concern. Secondly, the uranium-to-thorium ratio is different between the two samples with the sample from 4/93 approximating the naturally occurring ratio while the 12/93 sample has a substantially higher thorium content than expected. The variation in contaminant levels and ratios between these lots of carbonyl clearly demonstrates the need to address precursor quality control before production of the nickel components to a specific contaminant level can begin.

Unfortunately, the source of contamination in the nickel carbonyl is not clear from the limited results to date. LANL staff reported that the contamination seems to be present throughout the nickel, not just in the near surface region. This indicates that the uranium and thorium are present either in the carbonyl or in some aspect of the delivery system/reactor. We suggest that a study be performed by LANL in conjunction with your suppliers to determine the contamination levels at each step in the process. This would be done by purchasing several different lots of high-purity nickel powder, produced by the carbonyl process, and determining the contamination level by RNAA. This powder would then be converted back into nickel carbonyl and used to produce a nickel sample. Commercially available nickel carbonyl would also be used to make samples for analysis. By comparing the original contaminant level with the final values, the "cleanliness" of each step can be approximated. By performing these tests, LANL will be able to set realistic contaminant level goals for part production and determine if they will have to make special production runs of nickel carbonyl using certified starting material.

Production Reactor Design

During this project, we have demonstrated the higher deposition rate, improved precursor efficiency, and faster cycle times provided by the cold-wall CVD reactor. These benefits compel the use of cold-wall reactors for producing larger quantities of all of the components for the SNO Program. A general description for each of the reactors needed for each component is provided in the following sections.

1.5 Meter Tube Reactor. The design we have developed for the production-scale reactor takes into account the needs of a manufacturing environment, and it is expected between two and five of the systems would be necessary to produce the hundreds of meters of tubing needed for the SNO facility. The basic system configuration (Figure 1) would be modified for the 1.5-meter-long tubes. The reactor consists of a 304 SS vacuum chamber with cooling coils on the external surface. The mandrel will be heated using a three-zone insertion heater to produce a cold-wall and hot-mandrel reactor. One of the problems we faced during the bench-scale program was a non-uniform coating thickness around the circumference and along the axis of the stationary mandrel. In the

production-scale reactor, we would incorporate mandrel rotation and multiple precursor injection points to address these problems. Both of these techniques are commonly used to improve coating uniformity.

A key aspect of manufacturing is the release technique for the 1.5-meter-long tubes. We have identified two types of mandrels for these tubes. One mandrel would be a simple thick-wall 304 SS tube, while the other consists of 4 pieces of 304 SS which can be collapsed inward for removal. A cross section of the collapsible mandrel is shown in Figure 3. The four pieces of the collapsible mandrel are held in place using end caps which pin together the sections. When the end caps are removed, mandrel Sections A and C are pushed towards the center and extracted. Once these sections are removed, a clearance of at least 0.03" exists between the 304 SS foil-wrap and mandrel Sections B and D. These sections can then be easily removed also. The 304 SS foil will be removed from the inside of the tube using a simple tool which is akin to a key for a canned ham. Obviously, the cost of fabricating the collapsible mandrel is much greater than for the simple thick-wall tube. We believe that the foil-wrap release method can be used with the thick-wall tube mandrel to provide easy removal of the nickel tubes. But, the collapsible mandrel has a lead time of at least 6 weeks and the time constraints for this effort may require that both types of mandrels be evaluated in parallel.

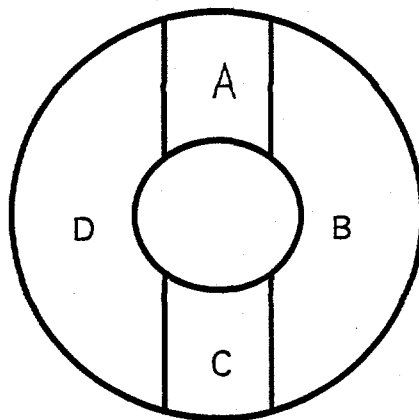


Figure 3. Cross-Section of Collapsible Mandrel

End Cap Reactor

The complex shape of the end cap and the need to produce a uniform coating present an unusual process problem. To provide a uniform substrate temperature, we would utilize a two-zone heater, which follows the end-cap shape, to heat a relatively thin mandrel. The end-cap mandrel would be 304 SS and would be expected to have a cross section of approximately 3/8-inch. One zone of the heater would be for the flat section of the mandrel while the other would be for the central cone. As with the 1.5-meter tubes, the mandrel would be rotated during deposition to mitigate the effect of any precursor flow variations. The mandrel would be suspended just above the heater to allow free rotation. Processing of the end caps would be performed in a quartz vacuum chamber. The gases would be injected using a radial distributor immediately above the mandrel. A nitrogen ballast would be introduced at the top of the chamber to prevent recirculation of the precursor gas stream.

With the cold-wall and hot-mandrel design of this reactor, we anticipate that the processing conditions for the end caps would be very similar to those of the bench-scale tubes we have produced. The major technical issue that must be addressed in this task would be the release of the end cap from the mandrel. Several options would be examined in this task. The relatively small contact area between the end cap and mandrel, compared to the bench-scale tubes, may allow direct release of the coating from a smooth mandrel. We would also examine a two-piece mandrel, where the cone threads into the flat section and may be used as an extraction tool.

Feed-Through Reactor

The small diameter of the feed-through tubes presents a different set of problems for releasing the coating from the mandrel. Since the use of the 304 SS foil as a release layer is not practical for this small a tube, we would evaluate the use of an aluminum mandrel for this component with the alloy to be selected after discussion with LANL. With a coefficient of thermal expansion of 25 ppm°K, versus 13 ppm°K for Ni, and 17 ppm°K for 304 SS, aluminum may allow direct removal of the feed through by immersing the coated mandrel in liquid nitrogen. We would prefer to make approximately 3- to 4-inch-lengths of the feed throughs, but if this high aspect ratio produces too

high an adhesion to remove the feed throughs, we would process shorter lengths.

Processing of these feed throughs would be performed in a small-diameter quartz chamber similar to those we have used for the prototype components. We would use a radio-frequency generator to inductively heat the aluminum mandrel and we would also rotate the mandrel to improve the coating thickness uniformity.

Sheet Stock Demonstration

Two options for producing the foil exist. In one option, a rectangular chamber would be constructed with heating elements on two of the interior walls. The stainless steel foil could be held against these heating elements, and the coating deposited onto the foil. The foil would then be peeled off of the nickel. The other option, which has already been shown to be effective, would be to use the existing bench-scale tube reactor and mandrel to form both the 0.003-inch-thick and 0.015-inch-thick foils on the 304 SS foil wrap on 2 inch diameter mandrels. In this project, we have been able to produce foils 6 inches wide and approximately 12 inches long in this manner. The foils were formed by depositing the nickel onto the 304 SS foil-wrap and then shearing the coating. The 304 SS foil was then peeled off the nickel. This technique would likely cost less than building a new reactor, and the foils can be flattened, if needed.

SUMMARY AND CONCLUSIONS

Summary

During this project, we achieved the following:

Modified the basic CVD nickel carbonyl system to a cold-wall reactor configuration.

Improved the precursor efficiency from less than five percent for the hot-wall CVD system to approximately 40 percent for the cold-wall system.

Reduced the deposition time for a 0.01-inch-thick coating from between 8 and 12 hours to 2 hours.

Developed and demonstrated a novel release technique for the 2-inch-diameter tubes that should substantially reduce production costs and which is applicable to manufacturing some of the other parts for the SNO Program also.

Produced and delivered to LANL a 2-inch-diameter by 8-inch-long CVD nickel tube.

Produced and delivered to LANL a 6-inch-wide by 12-inch-long CVD nickel foil deposited onto 0.001-inch 304 SS foil.

Developed reactor concepts for each of the parts for the production phase of the project.

Conclusions

The following conclusions can be made from the results of this program

Structural nickel parts can be produced by cold-wall CVD in a cost-effective manner while retaining a very low levels of α -emitter contaminants.

The contamination source in the CVD nickel process must be identified (nickel source, carbonyl process, or reactor systems) and controlled before setting contamination specifications for production parts. Without this control, a fixed-price production effort presents a high degree of risk to both LANL and the manufacturer.

The limited, and decreasing, number of nickel carbonyl producers limits the number of potential bidders on production tasks and may increase costs.

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