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# Preparing Supported Raney Nickel Catalysts by Dip Coating

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TABLE

# PREPARING SUPPORTED RANEY NICKEL CATALYSTS BY DIP COATING

by

L. L. Oden,[1] P. E. Sanker,[2] and J. H. Russell[1]


## ABSTRACT

The Bureau of Mines is conducting research to develop methanation catalysts for converting synthesis gas derived from coal to synthetic natural gas. This report describes a method to prepare supported Raney nickel coatings by dipping screen-covered nickel sheet in molten aluminum-nickel alloy. Coatings were formed at 1,050° C that were comparable in thickness, composition, microstructure, and catalytic properties to flame-sprayed commercially prepared Raney nickel.

A molten salt comprising cryolite-8 wt-pct LiF was employed over the molten metal bath to clean and preheat the substrates, to protect the metal bath from oxidation, and to heattreat the coated specimens. Immediately following heat treatment, specimens were quenched to 700° C in a molten salt bath containing $CaCl_2$-34.5 wt-pct NaCl, which also functioned to remove the insoluble occluded fluoride salt.


## INTRODUCTION

Binary alloys of aluminum and nickel in the composition range 30 to 50 wt-pct Ni are commonly called Raney (registered trademark of W. R. Grace and Co.) nickel alloys. However, in this study, the term is limited to a common commercial alloy containing 42 wt-pct Ni and 58 wt-pct Al. Raney nickel catalyst is obtained by selectively leaching (activating) most of the aluminum from the alloy using aqueous caustic solution.

The alloy is usually used in powdered form, although recently Goldberger (2)[3] applied Raney nickel alloy on suitable support materials by flame spraying. The alloy was activated in place to provide a supported catalyst coating. Haynes (4) also employed thermal spraying to deposit Raney nickel alloy onto the inside surfaces of stainless steel heat exchanger tubes to prepare the tube wall reactor (TWR) methanator. Forney (1) thermally sprayed Raney nickel

[1]Research chemist.
[2]Chemist.
[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

onto parallel plates of stainless steel to construct the hot gas recycle (HGR) methanator. Both TWR and HGR were designed to methanate synthesis gas derived from coal in the Bureau's Synthane coal gasification demonstration plant.

Raney-type catalysts supported on Raschig rings, Berl saddles, or other shapes are potentially useful in fixed beds where it is desirable to avoid the filtration step that follows conventional usage of powdered catalysts in liquid systems. Such shapes are not readily coated by thermal spraying, but may be coated by a slurry technique described by Mason (8) or a multistage process described by Larson (6) that requires deposition of nickel and aluminum on a suitable support followed by diffusion to form a Raney-type alloy on the surface.

Dip-coating a suitable support in a molten alloy may also be a useful method for coating small or irregular shapes, and such a method is alluded to by White (9). It was the object of this investigation to develop the dip-coating technique as a means to prepare Raney-type catalyst coatings. The study initially was sponsored by the Bureau of Mines and now is sponsored by the Energy Research and Development Administration. The Bureau is conducting the work at its Albany (Oreg.) Metallurgy Research Center.

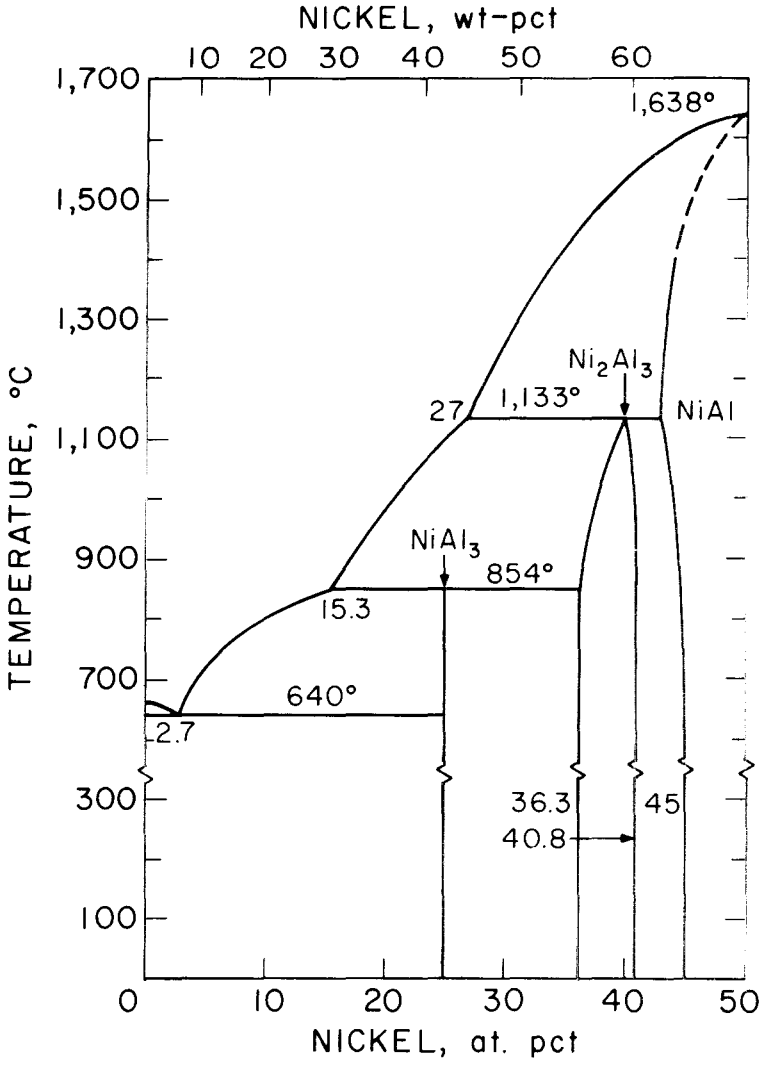


FIGURE 1. - Aluminum-nickel phase diagram.

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The authors wish to acknowledge W. L. O'Brien of the Albany Metallurgy Research Center for metallographic assistance and Michael Baird of the Pittsburgh (Pa.) Energy Research Center for performing the methanation tests.

CATALYST DESCRIPTION

The goal of this study was to prepare a Raney alloy coating comparable in thickness (0.5 mm), composition, and catalytic properties to flame- or plasma-sprayed commercial Raney nickel alloy. Therefore, it was appropriate to examine the Raney alloy metallurgically before and after thermal spraying.

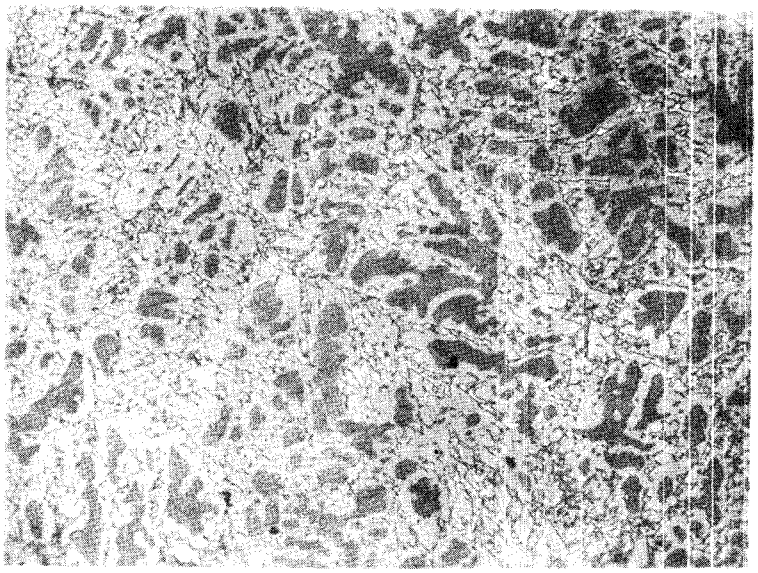

FIGURE 2. - As-cast Raney nickel (X 250).

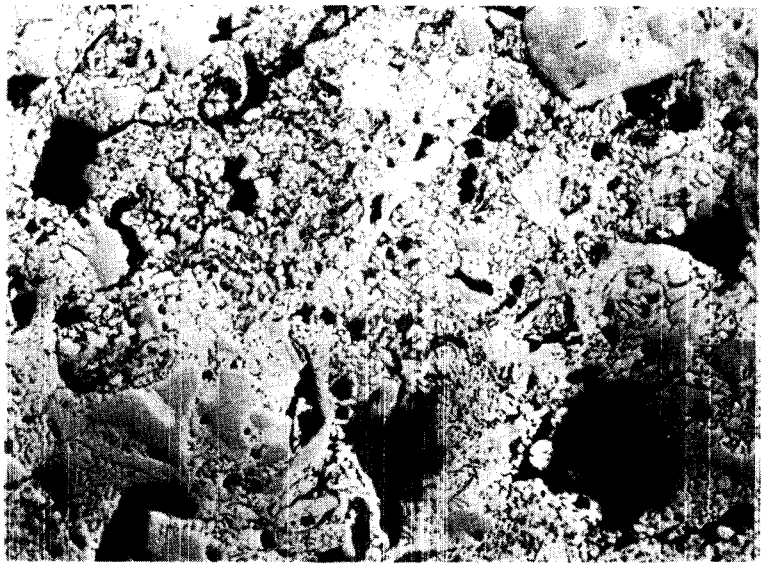

FIGURE 3. - Flame-sprayed Raney nickel (X 250).

Raney nickel alloy (expressed in atomic percent) is 25 at. pct Ni, which is the composition of the intermetallic compound $NiAl_3$. Figure 1, the Al-Ni equilibrium diagram (3), reveals that $NiAl_3$ is completely molten at about 1,100° C, and forms upon cooling by a peritectic reaction between $Ni_2Al_3$ and the liquid at 854° C. The peritectic reaction is generally incomplete at all finite cooling rates, resulting in three phases in the as-cast microstructure shown in figure 2. The optically dark phase is $Ni_2Al_3$, which appears as small irregular islands. Surrounding the $Ni_2Al_3$ is the lighter $NiAl_3$ phase, which is formed by peritectic reaction at 854° C. The peritectic was obviously incomplete, and the remaining unreacted liquid solidified at 640° C as the Al-$NiAl_3$ eutectic, which is the optically light phase.

Flame- or plasma-sprayed Raney nickel alloy is similar microstructurally to as-cast material except for the increased porosity, as shown in figure 3.

The relationship between catalytic activity and the phase assemblage in the alloy prior to leaching is not well documented. However, it is generally agreed that $NiAl_3$ is the desired phase based on the relative rates of activation of the nickel aluminides. The $NiAl_3$ is activated more readily than the $Ni_2Al_3$.

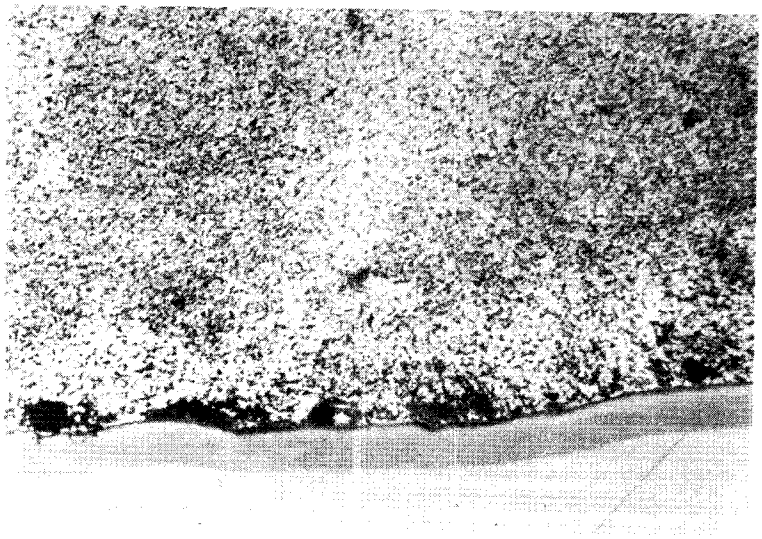

FIGURE 4. - Diffused aluminum-nickel interface after 50 min at 600° C (X 250).

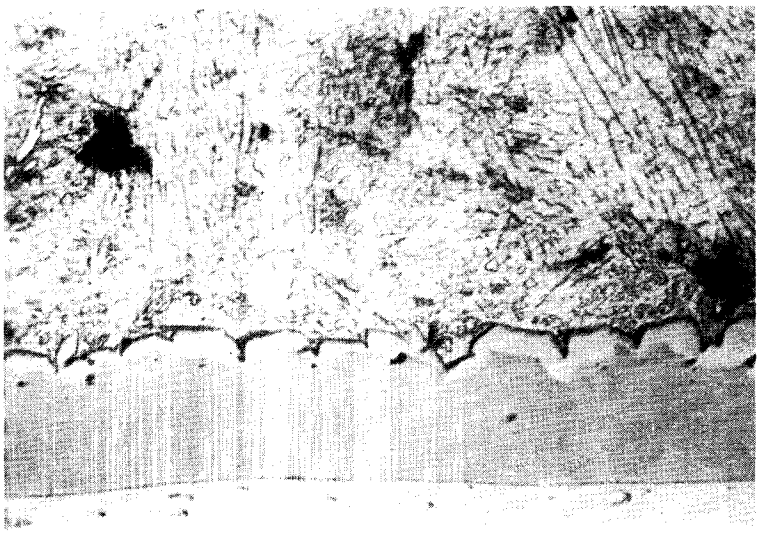

FIGURE 5. - Diffused aluminum-nickel interface after 90 min at 660° C (X 250).

## EXPLORATORY STUDIES

The patent of Larson (6) describes a method wherein nickel and aluminum are deposited onto a suitable substrate and then reacted at temperatures below the melting point of aluminum to prepare a Raney alloy coating. The coating was subsequently reacted with aqueous caustic solution to form an active supported Raney catalyst. Similar diffusion studies were conducted in the present investigation using nickel sheet that had been roll-bonded to aluminum or dip-coated in molten aluminum at 700° C. The former method of preparation was preferred for diffusion specimens to avoid the complicating interaction of nickel and aluminum during dip coating. Bonding between nickel sheet (1.6 mm) and aluminum sheet of the same thickness was achieved in the temperature range 400° to 600° C with a single pass through the rolls at 10- to 20-pct reduction, provided that all mating surfaces were clean and air was excluded during heatup. This was accomplished by welding the exposed edges of the oversize aluminum sheets. Steel or stainless steel plates at the rolling temperature were required between the rolls and the Al-Ni-Al pack to delay cooling of the pack by the cold rolls. Multiple passes through the rolls resulted in rupture of the Al-Ni bond at the brittle interface.

Small specimens of the bonded material were then heattreated at temperatures from 450° to 660° C, and the diffused interfaces were observed metallographically. The nickel substrate appears at the bottom of figures 4 and 5, which illustrate the structures observed at 600° and 660° C, respectively. The optically dark layer adjacent to the nickel is $Ni_2Al_3$, and the next lighter phase is $NiAl_3$. Unreacted aluminum is the uppermost phase in figure 4. The upper phase in figure 5 is the Al-$NiAl_3$ eutectic; observation indicates that the surface layer on this specimen was molten at the heat-treating temperature. The point of interest is the relative thickness of the $Ni_2Al_3$ and $NiAl_3$ layers in the two specimens. It is apparent that solid-state diffusion favors the formation of $Ni_2Al_3$, which is not the desired phase. This observation was further substantiated by other specimens that were heattreated for up to 90 hours. It was concluded that coatings formed by diffusion at temperatures below the melting point of aluminum are clearly not comparable to flame- or plasma-sprayed Raney nickel.

## DIP COATING

The molten metal for dip-coating studies was contained in a graphite crucible which was protected from oxidation by a stainless steel can. The annular space between the top of the can and the top of the crucible was stuffed with fibrous insulation to restrict the circulation of air, and the can was not allowed to touch the crucible. The crucible was heated in a Globar[4] resistance element furnace.

Protection of the metal bath was provided by a molten salt cover comprising cryolite-8 wt-pct LiF. That combination of salts was selected for its melting range (800° to 900° C) and solubility for the oxides of aluminum and nickel. The 6-inch thick salt cover also functioned to preheat the substrate prior to dip coating.

Also applicable was cryolite-25 wt-pct LiF-25 wt-pct NaCl, which is a useful remelt flux in the aluminum industry. The ternary mixture has less capacity for oxides but melts at lower temperature than the cryolite-8 wt-pct LiF.

Numerous borate and fluoborate salt mixtures chosen on the basis of their melting points were also studied, but all were found either to react with the metal bath or to be excessively volatile.

Exploratory dip-coating tests were made using a molten Raney nickel bath at 1,150° C and iron, nickel, and stainless steel substrates. The substrates were preheated for 30 sec in the protective molten salt cover and then submerged for 10 sec in the Raney nickel. Rapid contamination of the melt was observed for the iron and stainless steel substrates, and the molten metal drained from the surface of all three substrates to leave a very thin layer (0.03 mm) which then oxidized severely upon cooling in air. It was apparent from these tests that only nickel was applicable for substrates and that

[4]Reference to specific equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

lower dipping temperatures would be advantageous to reduce oxidation. The problems of increasing coating thickness and controlling the dissolution of the substrate were also identified.

## Increasing Coating Thickness

Embossed and perforated nickel sheet was dip coated in aluminum at 700° C in attempts to retain thicker coatings. Nickel sheet embossed with a rectangular array (0.25-mm-deep diamonds on 0.5-mm centers) retained the equivalent of 0.15 to 0.2 mm of Raney nickel. Actually, the indentations in the textured sheet and the holes in the perforated sheet were filled with molten material. The depth of the coating remained unchanged.

Nickel screen (16-mesh with 0.3-mm wire) was then attached by spotwelding to flat nickel sheet, and a series of specimens was dip coated in aluminum from 700° to 1,050° C. The experimental conditions are listed in table 1. Retention at all temperatures equaled or exceeded the target thickness of 0.5 mm, and with the use of double screen, thicknesses up to 1 mm were obtained. Each specimen was preheated for 30 sec in the molten salt cover, lowered into the molten aluminum for the time indicated, and then raised into the molten salt for heat-treatment periods ranging from 2.5 to 60 sec to allow nickel to dissolve into the molten layer. Specimens were then transferred to another molten salt bath at 700° C and allowed to air-cool to room temperature. The function of the salt bath at 700° C ($CaCl_2$-34.5 wt-pct NaCl) was twofold: to cool the specimen quickly through the temperature region in which most oxidation occurs, and to cool the specimen quickly to below 854° C to minimize $Ni_2Al_3$ formation in the molten layer. The water-soluble chloride salt bath also effectively removed the insoluble fluoride salt and facilitated cleanup of the specimens. The $CaCl_2$-NaCl ratio is the eutectic composition and melts at 500° C (7). The experimental parameters and results obtained for specimens considered optimum at each temperature are listed in table 1. Note that the dipping and heat-treatment times decrease significantly with increasing temperature.

TABLE 1. - Dip-coating[1] screen covered[2] nickel sheet in aluminum

| Specimen | Temperature, ° C | Time in Al, sec | Heattreat time, sec | Retention, mm |
|---|---|---|---|---|
| 1..... | 700 | 15 | 30 | 0.66 |
| 2..... | 815 | 5 | 10 | .55 |
| 3..... | 870 | 2 | 5 | .62 |
| 4..... | 970 | 2 | 5 | .57 |
| 5..... | [3]1,050 | 1 | 2.5 | .55 |
| 6..... | 1,050 | 1 | 2.5 | .55 |

[1]Preheated 30 sec in molten salt cover prior to dipping in Al.
[2]16-mesh screen, 0.3-mm nickel wire.
[3]Cooled from 1,050° C in air.

Figure 6 illustrates the microstructures of the surface layers obtained under the conditions listed in table 1. The microstructures at 700° and 815° C, which are below the $NiAl_3$ formation isotherm, comprise in order from

(1) 700° C (2) 815° C (3) 870° C (4) 970° C (5) 1,050° C, air-cooled (6) 1,050° C

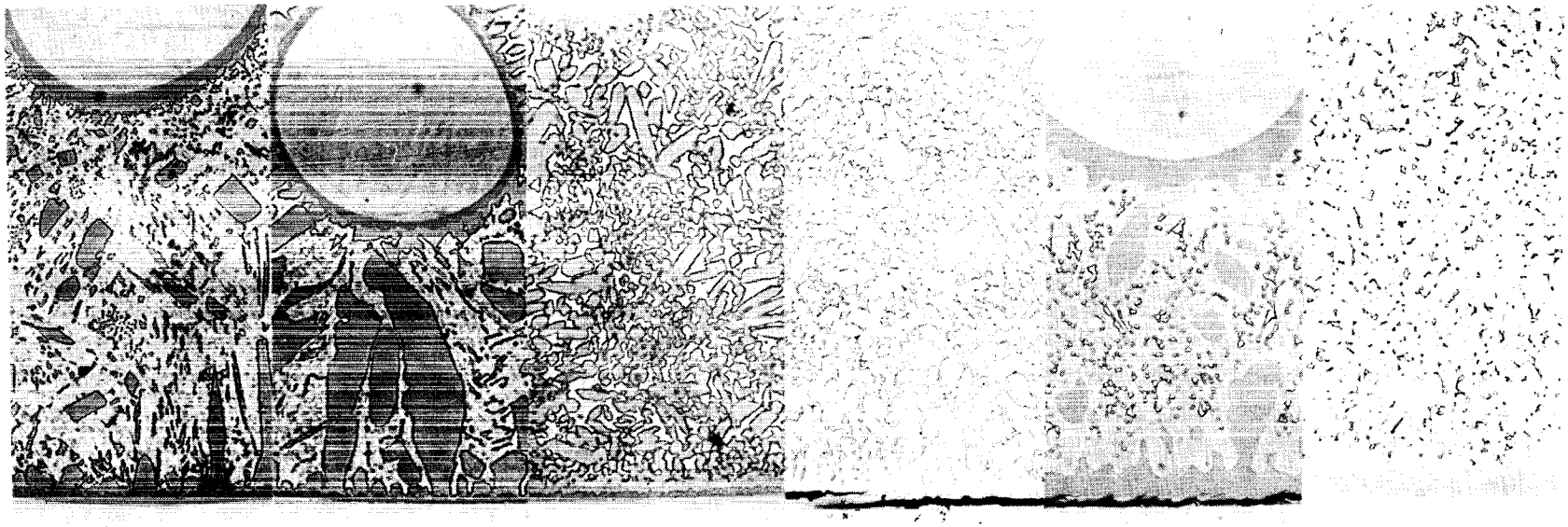

FIGURE 6. - Screen-covered nickel sheet dip-coated in aluminum from 700° to 1,050° C (X 250).

the bottom of the photograph the nickel substrate, a narrow band of $Ni_2Al_3$ (formed by solid-state diffusion of aluminum into nickel), an adjacent layer of $NiAl_3$ (formed by solid-state diffusion and by solidification from the melt), and a thick outer two-phased region of proeutectic $NiAl_3$ and eutectic.

The specimen formed at 870° C, which is above the $NiAl_3$ peritectic isotherm, is markedly different. $NiAl_3$ is not a stable solid phase at temperature but formed from the melt during cooling. The function of the rapid quench to 700° C is apparent in this and subsequent specimens in that the time spent in the temperature range in which $Ni_2Al_3$ forms is minimized, and therefore the compound forms as fine crystallites that are consumed in the peritectic reaction to produce $NiAl_3$. The proportion of $NiAl_3$ increased with increasing temperature because the molten surface layer becomes progressively richer in nickel following the liquidus curve. Specimens 4 and 5 were flexed slightly prior to mounting to initiate separation of the coating. Note that failure occurred within the narrow band of $Ni_2Al_3$. Specimen 5 illustrates the effect of air cooling at a less rapid rate. The large crystallites of $Ni_2Al_3$ were formed during cooling and were not consumed in the peritectic reaction at 854° C.

The fraction of $NiAl_3$ clearly increased with increasing temperature, and the specimen treated at 1,050° C was nearly ideal. Therefore, all subsequent dip-coating tests were done at that temperature.

## Dissolution Rate of Nickel in Aluminum-Nickel Alloy

The rapid rate of dissolution of nickel in aluminum, particularly at high temperature, required very short dipping times (1 sec at 1,050° C). Such times were nearly impossible to reproduce experimentally due to the length of the samples and timing of the hand-held support. For that reason the nickel content of the melt was increased as a means to slow the dissolution rate.

Nickel coupons 25 mm by 50 mm by 1.6 mm were preheated 30 sec at 1,050° C in the molten salt layer that covered the melt and then lowered into the melt for dipping periods of 10 to 60 sec. Some nickel was dissolved from each specimen, and additional nickel was added periodically to increase the concentration to a final value of about 35 wt-pct. Following the series of tests, the melt composition was computed from the weight loss of the coupons and the nickel added at specific intervals. The final computed bath composition (35.42 wt-pct Ni) agreed well with the analysis of the ingot (35.73 wt-pct Ni).

The dissolution rate was linear as shown in figure 7. The best fitting straight line computed by the method of least squares is given by $R = 14.2 - 0.37\ P$, where the units of R and P are milligrams per square centimeter per second and weight-percent nickel, respectively.

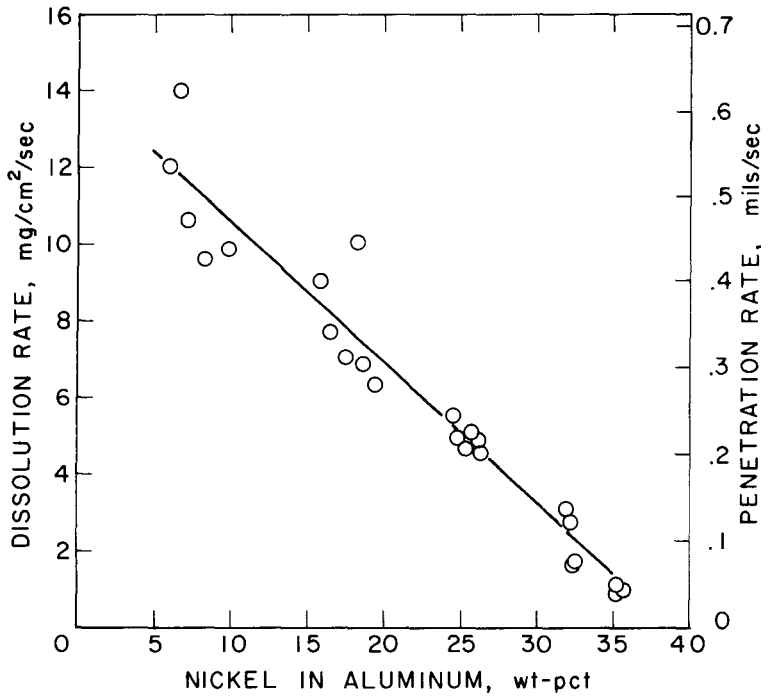


FIGURE 7. - Dissolution rate of nickel in aluminum-nickel alloy.

The dissolution rate at nickel concentrations of 30 to 35 pct is such that dipping periods of 5 to 60 sec are permissible. A standard timing sequence was adopted for all future tests: 30 sec preheat in the molten salt, 5 sec in the Al-30Ni melt, and 10 sec in the molten salt for heat treatment. A flow diagram for the dip-coating process is given in figure 8.

## Dip-Coating Scaleup

Substrate shapes other than flat sheet were dip coated in anticipation of practical application. A large crucible was prepared, and screen-covered specimens up to 150 mm long were dipped (1,050° C, 30 pct Ni in melt) to determine the

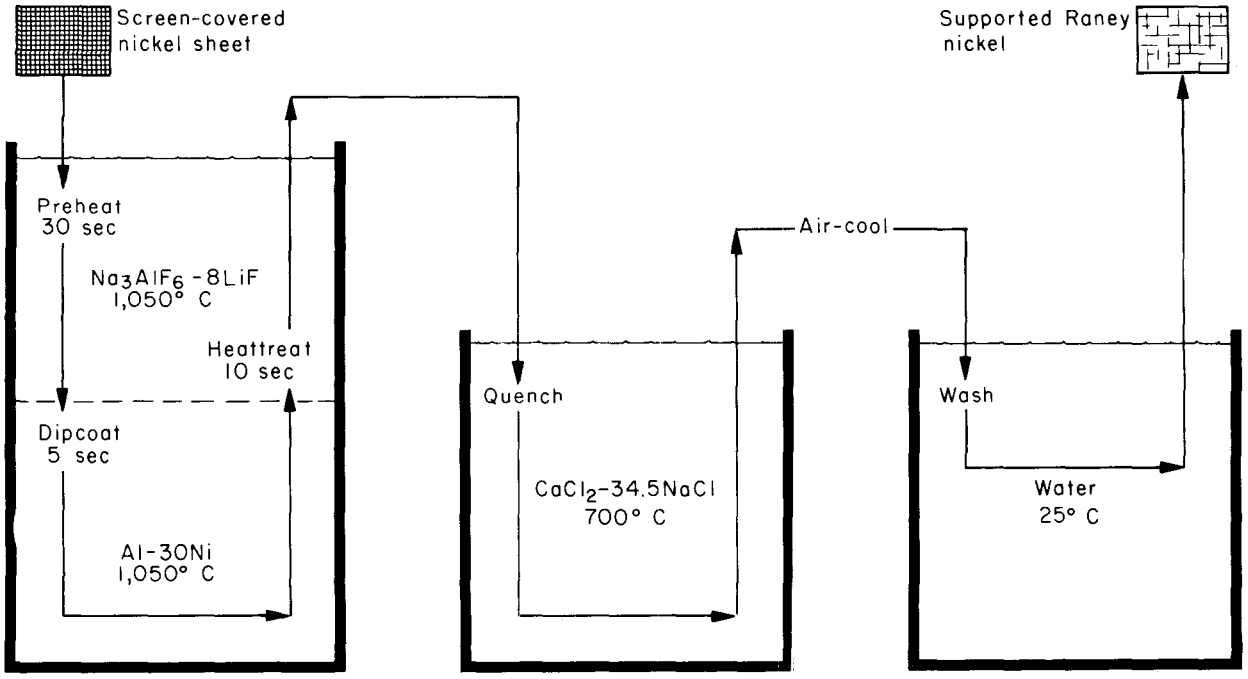


FIGURE 8. - Flow diagram for the dip-coating process.

relation between filling of the screen and vertical height. It was found that about 65 mm vertical rise was the maximum to maintain complete filling of the screen. Figure 9 illustrates some of the coated specimens, which included 50-mm by 150-mm plane sheet, 25-mm and 50-mm-diameter by 150-mm-long cylinders with screen on the inside or the outside, and 50-mm by 150-mm cross shapes with screen on all surfaces. The long dimension of the above specimens was maintained horizontal during dip coating.

Some distortion of thin sheet specimens can occur if coatings are not uniform on both sides. The coefficient of thermal expansion at 550° C for Raney nickel as measured by Henry (5) in this laboratory is $13.1 \times 10^{-6}$° $C^{-1}$, whereas the value for nickel is $16.3 \times 10^{-6}$° $C^{-1}$. If planarity in a flat sheet is desired, then both surfaces must be covered with screen and coated equally. It should be noted that the coating is integral with the substrate but very brittle. Flexing the substrate will separate the coating with the fracture line following the $Ni_2Al_3$ phase adjacent to the nickel.

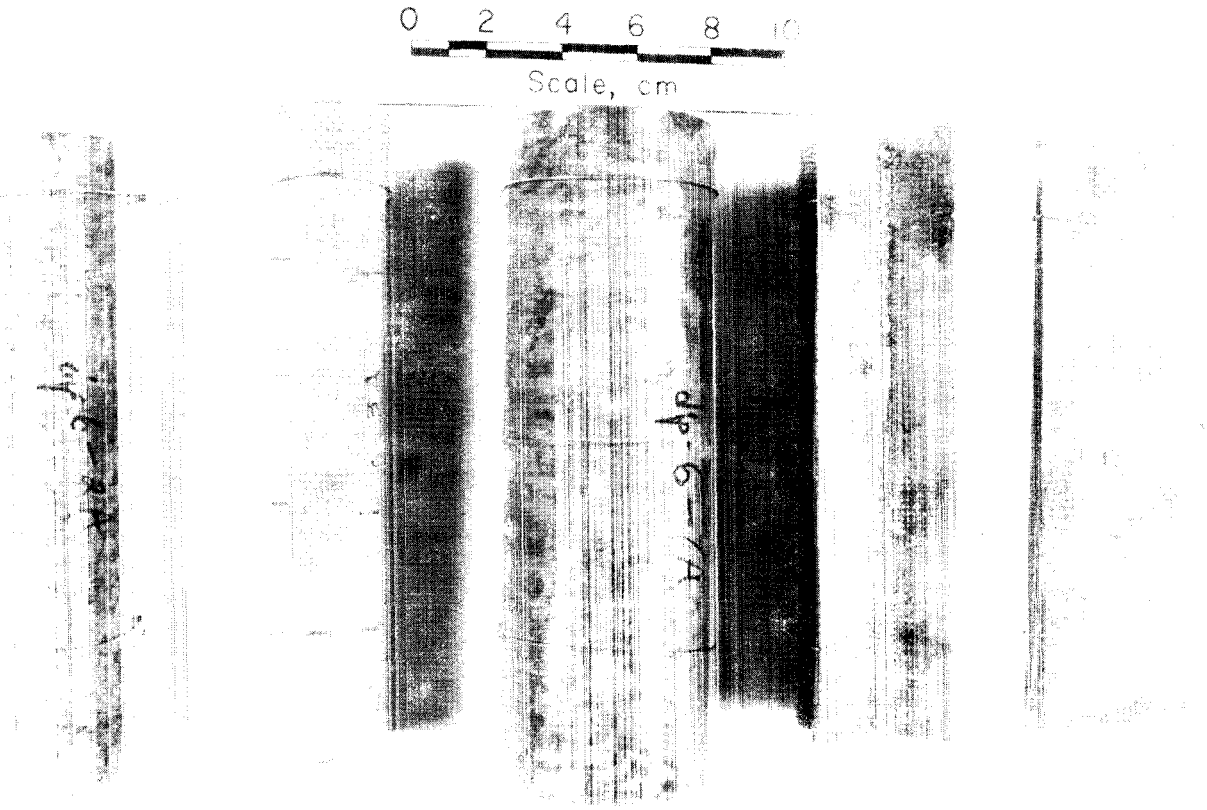


FIGURE 9. - Supported catalyst specimens prepared by dip coating.

## METHANATION

The methanation activity was measured for a screen-covered sample that was prepared according to the flow diagram on figure 8. A pulse microreactor method was used at 320° C with a total flow rate of 60 $cm^3$/min (STP) in a 0.635-cm-bore tube. Conversion of $H_2$ and CO (ratio 3:1) to $CH_4$ at atmospheric pressure averaged 92.6 pct (5 pulses) for a sample activated by leaching in 2 pct caustic for 2 hr at 60° C. Activation for 4 hr at 60° C reduced the activity to 85.8 pct (4 pulses), whereas 2 hr at 60° C followed by 1 hr at 90° C resulted in 93.3-pct conversion (3 pulses). These values are comparable to activities measured for flame-sprayed Raney nickel.

## DISCUSSION

Dip-coating nickel in a molten aluminum-nickel alloy was shown to be a viable method for producing supported Raney nickel catalyst. Embossed, perforated, and screen-covered nickel surfaces were investigated in attempts to improve the retention of the very fluid molten surface layer. Only the screen covered surface (16-mesh screen with 0.3-mm wire) retained coatings comparable in thickness to flame-sprayed material (0.5 mm). Coating must be done at high temperature (1,050° C) to obtain the requisite nickel content (35 to 42 wt-pct Ni) in the molten surface layer.

The rapid dissolution rate of the base metals in molten aluminum-nickel alloys precludes the use of all metals except nickel for preparing Raney nickel by dip coating. The dissolution rate for nickel decreases with nickel content of the melt at 1,050° C according to the relation $R = 14.2 - 0.37\ P$ where the units of R and P are milligrams per square centimeter per second and weight-percent nickel, respectively. Numerous supported catalyst shapes were prepared by dip-coating in aluminum-30 wt-pct Ni for 5 sec and heat-treating at the same temperature for 10 sec producing about 90 pct $NiAl_3$ in the catalyst layer.

The only fundamental limitation to the size of screen-covered objects to be coated is that the vertical rise must not exceed about 65 mm if complete filling of the screen is desired. That parameter, as determined with 16-mesh screen having 0.3-mm wire, may be changed with different screen or wire sizes.

Graphite crucibles were satisfactory for containing the molten metal and the cryolite-8 wt-pct LiF salt that protected the melt from oxidation. The molten salt also served to clean and preheat the nickel substrate prior to immersion into the molten metal bath and to heattreat the coated substrate after dip coating.

The proportion of phases in the coating is determined by both the composition and the thermal history. The composition was optimum in specimens dip-coated at 1,050° C in aluminum-30 wt-pct Ni for 5 sec and heattreated at the same temperature for 10 sec. The proportion of $NiAl_3$, which is the precursor to active Raney nickel catalyst, was enhanced by cooling rapidly from the heat-treating temperature to 700° C in a molten salt bath. The $CaCl_2$-NaCl eutectic composition (34.5 wt-pct NaCl) was satisfactory for that application, and in

addition, it dissolved the occluded water-insoluble fluorite salt. Removal of the chloride salt was then quickly accomplished in warm water.

The supported catalyst produced by dip-coating is integral with the substrate but very brittle. Flexing coated objects will separate the catalyst layer along the thin zone of $Ni_2Al_3$ which is adjacent to the nickel.

The dip-coating technique should be applicable to forming irregular supported catalyst shapes such as Berl saddles or Raschig rings as well as short cylinders and flat sheets. To minimize distortion in the final shape, all surfaces must be coated uniformly.

Promoters to Raney nickel, although not studied in this work, should be readily added to the melt or incorporated as alloying elements in the nickel substrate.

The catalytic activity (methanation) of dip-coated specimens was found to be comparable to that of flame-sprayed Raney nickel.

## REFERENCES

1. Forney, A. J., R. J. Demski, D. Bienstock, and J. H. Field. Recent Catalyst Developments in the Hot-Gas-Recycle Process. BuMines RI 6609, 1965, 32 pp.

2. Goldberger, M. (assigned to Catalytic Technology Corp., Manchester, Conn.). Raney Metal Sheet Materials. U.S. Pat. 3,637,437, Jan. 25, 1972.

3. Hansen, M. Constitution of Binary Alloys. McGraw-Hill Book Co., Inc., New York, 2d ed., 1958, p. 119.

4. Haynes, W. P., J. J. Elliott, A. J. Youngblood, and A. J. Forney. Operation of a Sprayed Raney Nickel Tubewall Reactor for Production of a High-Btu Gas. Preprints, Division of Fuel Chemistry Symposium, Am. Chem. Soc., v. 14, No. 4, September 1970, pp. 26-48.

5. Henry, J. L. Private communication, 1975. Available upon request from L. L. Oden or J. L. Henry, Bureau of Mines, Albany, Oreg.

6. Larson, F. G., Jr. (assigned to International Nickel Co., Inc., New York). Method for Producing Nickel Catalyst. U.S. Pat 3,846,344, Nov. 5, 1974.

7. Levin, E. M., C. R. Robbins, and H. F. McMurdie. Phase Diagrams for Ceramists, 1969 Supplement. American Ceramic Society, Columbus, Ohio, 1969, p. 302.

8. Mason, D. A. (assigned to Institute of Gas Technology, Chicago, Ill.). Supported Skeletal Nickel Catalyst. U.S. Pat. 3,448,060, June 3, 1969.

9. White, P. C. (assigned to Standard Oil Co., Chicago, Ill.). Preparation of a Raney Catalyst Surface. U.S. Pat. 2,583,619, Jan. 29, 1952.

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16. Abstracts

The Bureau of Mines is conducting research to develop methanation catalysts for converting synthesis gas derived from coal to synthetic natural gas. The present report describes a method to prepare supported Raney nickel coatings by dipping screen-covered nickel sheet in molten aluminum-nickel alloy. Coatings were formed at 1,050° C that were comparable in thickness, composition, microstructure, and catalytic properties to flame-sprayed commercially prepared Raney nickel. The study initially was sponsored by the Bureau of Mines and is now sponsored by the Energy Research and Development Administration.

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Methanation catalyst, development
Synthesis gas from coal
Synthetic natural gas conversion

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Raney nickel
Nickel

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