BUREAU OF MINES
Pittsburgh Coal Research Center
Pittsburgh, Pennsylvania 15213

DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE IN ALKALINE H_2-O_2 FUEL CELLS

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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE

IN ALKALINE H_2-O_2 FUEL CELLS

The objective of this project is the synthesis of interstitial compounds for increasing the efficiency of the oxygen electrode in alkaline H_2-O_2 fuel cells. The work is being carried out for the National Aeronautics and Space Administration with Mr. E. M. Cohn as technical monitor. Principal investigators are Sayeed Akhtar, C.T. Grein, R.C. Diehl, W.H. Ryback, and D. Bienstock.

Bureau of Mines
Pittsburgh Coal Research Center

Quarterly Report for the period ending June 30, 1967

Development of An Improved Oxygen Electrode for Use in Alkaline H_2-O_2 Fuel Cells

Summary

A total of 34 preparations were synthesized and shipped to Tyco Laboratories in this quarter. In addition, 130 samples were sent to other firms designated by the Technical Monitor of N.A.S.A. These preparations include:

(a) Powders of Ni, Co, 1Ni-1Ag, 1Ni-1Pd and 1Ni-1Ag-1Au obtained by reducing precipitated hydroxides of these metals;

(b) powders of Ni and 3Ni-1Co obtained by reducing nickel formate and a mixture of nickel formate and cobalt acetate;

(c) carbides of Ni, Co, 1Ni-1Ag, and 1Ni-1Pd prepared from reduced metals obtained in (a) and (b);

(d) nitrocarbides of Ni, 1Ni-1Ag and 3Ni-1Co;

(e) borides and mixed borides of Ni and Co;

(f) carbides and nitrocarbides of 3Ni-1Ag, 1Ni-1Pd, and 1Co-1Ag-1Pd prepared from Raney alloys.

Introduction

The object of this project is to develop catalysts for the cathodic reduction of oxygen in alkaline H_2-O_2 fuel cells. The work is being conducted in cooperation with Tyco Laboratories Inc., and the materials under investigation are the interstitial compounds of transition metals, singly and in combinations, with carbon, nitrogen, boron and silicon. Samples of the preparations are also sent to other firms designated by the Technical Monitor of N.A.S.A. This report deals only with the preparation of these compounds; information of the efficacy of the preparations in laboratory tests may be obtained from the quarterly reports of Tyco Laboratories.

Experimental

A. Preparation of Precipitated Materials

(a) Mixed metal hydroxides

Mixed metal hydroxides were coprecipitated by adding an excess of sodium hydroxide to solutions of metal salts at 80°-90° C. The reaction mixture was agitated with a magnetic stirrer during the addition of the precipitant. Stirring and heating were continued until the mixture came to a boil. The precipitate was washed several times by decantation until the material became colloidally dispersed. At this stage, a weighed amount of NH_4NO_3 to give approximately 1 percent concentration of the electrolyte in the wash liquid was stirred into the suspension to break the colloid. The precipitate, on settling, was filtered on a Buchner funnel, dried at about 90° C, crushed to a fine powder and re-dried at 110° C.

The metal salts employed in this work were preferably nitrates. The nitrates of nickel and cobalt were purchased commercially and silver nitrate was prepared by dissolving a stock of splattered silver in nitric acid. Stock solutions of gold, platinum and palladium were prepared by dissolving the metals in aqua regia.

Coprecipitated hydroxides of the following combinations of metals, in the proportions shown below, have been prepared:

1.	3Ni-1Co	7.	1Ni-3Pd
2.	3Ni-1Ag	8.	3Ni-1Au
3.	1Ni-1Ag	9.	1Ni-1Au
4.	1Ni-3Ag	10.	1Ni-3Au
5.	3Ni-1Pd	11.	1Ni-1Ag-1Au
6.	1Ni-1Pd	12.	1Ni-1Au-1Pd

The hydroxides of the combination 1Ni-1Ag-1Au had to be prepared in two steps because of the presence of chloride ions in the solution of gold. The hydroxides of nickel and gold were coprecipitated first and washed free of chloride ions. The mixed hydroxide was then suspended in a solution of sodium hydroxide and the calculated amount of silver nitrate solution was added to it with vigorous stirring. The material was then washed, dried and crushed in the usual manner.

Preparations involving gold were treated with a 0.1 percent solution of $Ni(NO_3)_2$ in the final stages of washing, when the material tended to stay colloidal. The use of NH_4NO_3 with these preparations was avoided to eliminate the risk of forming gold azide.

(b) Preparations Involving Platinum

Since platinum is not precipitated as hydroxide from a solution of its soluble salt by interaction with NaOH, the following modified procedure was adopted for the preparations involving platinum. Nickel and/or other components were precipitated first in the usual manner, after which an excess of sodium formate was added to the hot reaction mixture to precipitate reduced metallic platinum on the finely dispersed particles of the hydroxide(s). Heating and stirring was continued until the reduction of platinum was complete. The material was then washed, dried and crushed in the usual manner. Preparations of the following composition have thus been prepared:

1.	3Ni-1Pt	3.	1Ni-3Pt
2.	1Ni-1Pt	4.	1Ni-1Au-1Pt

B. Reduction of Precipitated Materials

In earlier experiments the hydroxides of nickel and cobalt were reduced with hydrogen at 350° C for 3½ to 5 hours. X-ray analyses of the reduced materials indicated the hydroxides to have been reduced satisfactorily. However, all efforts to carbide the reduced powders by treatment with carbon monoxide at 250°-260° C were fruitless. Careful examination of the procedure reported by Hofer, Cohn, and Peebles [1] for the preparation of Ni_3C from nickel hydroxide indicated a significant procedural difference at one step only; nickel hydroxide was reduced by these workers at 275° C. It was suspected that at 350° C, the temperature employed in our experiments, the reduced materials so obtained were not amenable to reaction with carbon monoxide. Successful carbiding was subsequently obtained by reducing the precipitated materials at 275° C. A considerably longer reduction period is, of course, required at 275°C than at 350°C; in the experiments currently under progress, each preparation is reduced for 85 hours.

It was observed that preparations containing palladium are reduced by hydrogen even at room temperature. As soon as hydrogen is brought into contact with these materials, large quantities of water of reduction are released and the temperature of the bed rises rapidly. Precipitated materials containing palladium were treated with a mixture of CO_2 and H_2 until the initial phase of high activity had subsided, following which the reduction was continued with pure H_2 and the temperature was slowly raised to 275°C without any noticeable tendency for overheating. The reduction treatment at 275°C was then continued for the usual 85 hours. Preparations containing gold exhibited similar behavior but at a milder level; the reduction could be pursued with pure hydrogen even in the initial stages, albeit with proper ventilation to conduct the heat away from the bed.

Table 1 is a list of the precipitated materials that were reduced during the quarter.

TABLE 1.- Reduction of precipitated materials

Space velocity of H_2:   1000 hr^{-1}
Temperature: 275 °C
Time: 85 hours

Run no.	Composition of reduced material
*53R	1Ni-1Ag
56R	Ni
57R	1Ni-1Pd
59R	Co
60R	1Ni-1Ag-1Au

*The letter R signifies reduced metal.

C. Preparation of Carbides

The finely divided reduced materials were carbided with carbon monoxide at 250°-260° C. The technique and the apparatus employed for carbiding these materials were the same as described earlier (2) for the preparation of the carbides of iron from Raney iron. The temperature of the bed was raised to 250°C in gradual steps extending over several hours. This precaution eliminates the risk of a large sudden rise in temperature which causes excessive deposition of free carbon. Table 2 is a list of the reduced hydroxides that were carbided in this quarter. The duration of treatment with CO and the analysis of total carbon and free carbon are included in the table for each preparation. Supporting evidence for the formation of carbides was obtained by x-ray analysis.

D. Preparation of Nitrocarbides

Nitrocarbides were prepared from carbides by treating the latter with gaseous ammonia at 250°-260° C.

38NC - The carbide of 1Ni-1Ag obtained in 53C was treated with NH_3 at 260°C for 48 hours at an hourly space velocity of 1000.

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TABLE 2.- Preparation of carbides

| | | | | Chemical analysis, weight-percent | | |
Run no.	Charge[1]	Duration of carbiding, hrs.	Temp., °C	Total C	Free C	X-ray analysis
	Carbiding gas:		CO			
	Hourly space velocity:		100			
53C	1Ni-1Ag	5 102 106	160-250 250 260	1.92	0.12	Ni_3C, Ag
56C	Ni	6 102 36	160-250 250 260	0.94	0.20	Ni_3C, Ni
57C	1Ni-1Pd	6 37 103	160-250 250 260	1.19	0.95	
59C	Co	5 100	160-250 250			Co_2C

[1] Reduced precipitated/coprecipitated hydroxides.

E. Preparation of Carbides and Nitrocarbides from Organic Salts of Transition Metals

(a) 3Ni-1Co

50R - A mixture of nickel formate and cobalt acetate (3Ni-1Co) was prepared by slurrying nickel formate in an aqueous solution of cobalt acetate. The slurry was evaporated to dryness at room temperature, crushed and heated at 190°C for 17 hours. It was then reduced with hydrogen at 250°C for 27 hours at a space velocity of 1000 hr^{-1}.

50C - The reduced powder obtained in 50R was treated with CO at 160°-270°C for 5 hours, and 270°C for 97 hours at an hourly space velocity of 100. The product when analyzed for its carbon content showed total carbon: 12.8%, free carbon: 7.2%.

58C - The reduced powder obtained in 50R was treated with CO at 160°-260° C for 5 hrs, and at 260°C for 107 hours. Total carbon: 9.4%, free carbon: 3.8%.

36NC - The carbide obtained in 50C was treated with NH_3 at 260°C for 48 hours at an hourly space velocity of 1000. The nitrogen content of the nitrocarbide was 1.02%.

37NC - The carbide obtained in 58C was nitrocarbided by treatment with NH_3 at 260°C for 48 hours.

(b) Ni

54R - Nickel formate was decomposed in an oven at 190°C. The material was then reduced in a stream of hydrogen at 250°C for 85 hours at a space velocity of 100 hr^{-1}. X-ray diffraction pattern indicated the reduced metal to be cubic nickel.

54C - The reduced nickel obtained in 50R was treated with CO at 160°-250°C for 5 hrs, and at 250°C for 100 hours at an hourly space velocity of 100. X-ray analysis of the product gave the pattern of Ni_3C. (Chemical analysis: total carbon: 6.85%, free carbon: 0.57%. By inference, combined carbon: 6.28%. Calculated value for Ni_3C, combined carbon: 6.38%.)

F. Preparation of Catalytic Transition-Metal Borides

A search of the literature on the preparation of finely divided borides of iron, nickel, and cobalt has yielded four general techniques (3): Melt reduction, aqueous precipitation, gas-phase reaction, and fused-salt electrolysis. All have possible application in preparing the catalytic materials desired.

(a) Melt Reduction

Melt reduction, using a metal oxide or salt, B_4C or pure boron, and carbon, as well as direct metal-boron fusion, typically yield a brittle bulk solid (4,5). Hoke (6) has reacted $NaBH_4$ and metal halides at 150°C under an inert gas. The product mass, after leaching with methanol-water, gave a powdered boride. Whether material prepared in this way would have a sufficiently large specific surface area to serve as a catalyst would have to be determined.

E.I. DuPont DeNemours and Co. has patented a process for producing powdered borides of 1-250 micron particle size and large specific surface area (7). A mixture, consisting of a salt of the transition metal, an alkali boride or similar boron-containing compound, and an alkali metal, is heated in fused alkali halide under argon. The resulting boride is recovered by dissolving the cooled salt mass, leaving a fine, flocculent precipitate. This process would seem to be well suited to our requirements; however, it may be significant that, while the patent specifically mentions preparation of compounds of seven transition metals, no use of iron, cobalt, or nickel is reported.

(b) Aqueous Precipitation

Schlessinger, et al. (8), report that $NaBH_4$ and metal halides react in aqueous solution to give finely divided borides. Several workers (9,10,11) have found these materials to possess good catalytic activity for hydrogenation, and Jasinski (12) has used NiB_2 prepared in this way as a hydrogen catalyst in H_2-O_2 alkaline fuel cells. A difficulty with this method of preparation is that the material obtained is subject to slow decomposition on exposure to air or water and that such reaction sharply decreases the material's catalytic activity (9,10).

(c) Gas-Phase Reactions

Gas-phase borations reported are of two types. The method less feasible for our purposes treats BCl_3 with vaporized metal halide in a hydrogen atmosphere at the surface of a hot tungsten filament (400°-2000° C)(13). The boride deposits on the filament in microcrystals, the lowest temperatures and highest pressures producing virtually amorphous material. Two possible uses of this technique are direct coating of an electrode matrix with catalytic boride (such a coating also serving to protect the matrix from chemical attack) and deposition of boride in layers sufficiently thick to be flaked off.

A more feasible gas-phase reaction involves attack of BCl_3 on finely divided metal in a hydrogen atmosphere at about 1000°C (14). Particles of 1-2 microns have been treated in this way. The desired material is present only as a surface coating, the bulk of the metal (about 90%) is unreacted.

(d) Fused-Salt Electrolysis

Fused-salt electrolysis, like melt reduction, is generally used to prepare bulk solid material (15,16). However, Stern, et al. (17) have reacted metal carbides and B_4C in a NaCl bath under argon, with a 1.3 v. potential. The yield was a brittle sponge which, after washing, could easily be crushed to a powder. It might be possible to crush this material sufficiently to obtain the high specific surface area required.

Of the methods described, the simplest, and the one of proven value in catalyst preparation, is the solution technique of Schlessinger (8). It was decided to concentrate initial efforts on this method so as to obtain materials suitable for testing as rapidly as possible. It was further decided that a modification of the gas-phase technique of Andrieux (14) would be explored when the limited versatility of the solution technique was exhausted.

According to Schuele and Deetscreek (18), $NaBH_4$ and salts of the Group VIII metals react according to the following stoichiometry,

$$8NaBH_4 + 4NiSO_4 + 18H_2O \rightarrow 2Ni_2B + 6H_3BO_3 + 4Na_2SO_4 + 25H_2. \qquad (1)$$
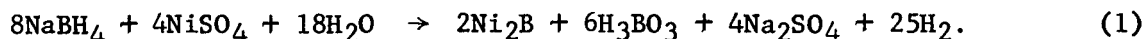
The product boride decomposes slowly in water; the wet powder reacts with air to give a catalytically inactive material (9), and is pyrophoric when dry (8). Thus reactions were carried out under nitrogen atmosphere. The product still damp and under nitrogen was transferred to absolute ethanol, dried in a vacuum and stored under CO_2.

Schlessinger (8) has observed that the Group VIII borides are efficient catalysts for the decomposition of $NaBH_4$ by the reaction

$$2H_2O + NaBH_4 \rightarrow NaBO_2 + 4H_2. \qquad (2)$$
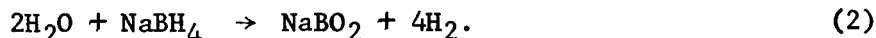
Thus, a small amount of boride initially formed by Reaction (1) can rapidly convert the remaining $NaBH_4$ to metaborate and H_2 with little or no further boride production. This undesirable result was prevented by kinetic control of the reaction; $NaBH_4$ solution was added dropwise to an excess of metal ion, strongly favoring Reaction (1) over (2).

In practice, one liter of aqueous solution, 1.8 M in total metal ion concentration, was stirred in a three-necked flask under a N_2 flow of 2 ft^3/min. A 500 ml. quantity of 7.2 M $NaBH_4$ was added dropwise. During the addition, a voluminous black precipitate formed, considerable amount of H_2 gas was evolved, and the temperature of the reaction vessel rose to about 60° C. When addition was complete, the reaction mixture was stirred for 20 minutes, giving a total reaction time of 45 minutes.

The precipitated boride was recovered by drawing off the super-
natant liquid with a fine porosity filter stick. In general, the
supernatant liquid after reaction still showed a definite color
characteristic of the metal ion(s) initially present; this indicates
loss of some $NaBH_4$ by direct H_2 production (Reaction 2). The product
boride was slurried 4 times with 1 liter portions of distilled water
and twice with 500 ml dry ethanol. During the entire wash procedure,
the material was maintained under N_2 in the reaction vessel. A third
portion of dry ethanol was used to slurry the boride into a temporary
storage container. Final drying was accomplished by vacuum dis-
tillation to 100°C. The material was then transferred under vacuum
to the dry box and stored under CO_2.

For borides in which cobalt was the principal metal present it
was impossible to use a filter stick, since the extremely fine pre-
cipitate rapidly plugged the filter. These materials were filtered
in air with a Nalgene filter covered with a paper mat. While not
completely retentive, this device did trap the major portion of the
material. During filtration, the liquid level was not permitted to
drop below the surface of the precipitate in the funnel, preventing
exposure to air. Final drying was done in the same manner as with
the more granular precipitates.

Using the above techniques, a series of borides was prepared,
as shown in table 3. In all but B-7, the product was substantially
in excess of the 116 g predicted from stoichiometry. There seems to
be a significant amount of contaminant present, probably metallic Ni
and/or Co and Na_2SO_4. Analysis of total boron content and calculation
of the percentage of M_2B present, based upon the hypothesis that all
boron detected is in the form M_2B, confirms that substantial amounts
of impurity were present in almost all cases. The single exception,
B-7, appears to have given a near-stoichiometric quantity of material
with proper boron content, although some material was lost on filtration.

X-ray powder diffraction studies shows an amorphous material in all
cases. Hofer (19) was able to obtain x-ray patterns for Ni_3B and Ni metal
upon heat-treatment of solution-precipitated nickel boride. Sample B-8A,
which represents material which was briefly exposed to air in the dry
state, and which became quite hot, showed a pattern for Ni_3B, corre-
lating with Hofer's work.

TABLE 3.- Summary of Boride Preparations

Sample no.	Initial moles		Yield, grams	Boron, percent	M_2B, percent[1]	X-ray analysis
	Ni	Co				
B-6	1.8	-	150.43	5.20	61.2	Amorphous
B-7	-	1.8	107.90	8.66	100	Amorphous
B-8	0.9	0.9	142.71			Amorphous
B-8A	0.9	0.9	64.81	6.72	79.1	Ni_3B
B-9	1.35	0.45	120.20	6.50	76.5	Amorphous
B-18	0.9	0.9	146.93	4.35	51.1	
B-20	0.45	1.35	160.34	3.75	44.0	

[1] Assumes all boron present as M_2B.

Attempts to prepare ferrous boride, preparation of which by solution techniques is somewhat controversial, have so far been unsuccessful. Further work is being done to obtain this material. Also being considered is the preparation of intimate mixtures of Group VIII borides and finely divided noble metals. In principle, the noble metal ion should be reduced to the free metal by $NaBH_4$ under the same conditions used for boride precipitation.

Construction has begun on a gas-phase reactor for surface boridation using a BBr_3-H_2 atmosphere ([20]). When this is operational, attempts will be made to prepare a greater variety of borides than is possible by the solution technique.

G. Preparation of Nitrides of Transition Metals

In continuation of the work described earlier (21), the possibility of nitriding nickel and cobalt by treatment with ammonia, nitrogen or a mixture of the two in a pressurized vessel has been investigated further. Figure 1 is a sketch of the apparatus employed in these experiments. The reaction vessel was made of stainless steel and was tested hydrostatically for pressures up to 4000 psig. The rupture disc was set at 2600 psig and this represented the upper limit of the working pressure in these experiments.

*NLA-5 - The reactor was charged with 7.9 g of reduced Raney nickel, containing 0.7% nitrogen from a previous experiment, 120 psig N_2, and an excess (approximately 150 ml) of liquid NH_3. The reactor was maintained at 97°-99° C in a hot water bath for 21 hours. The pressure varied between 950 to 1030 psig. The bomb was then cooled to room temperature, the pressurized gases released, flushed with nitrogen, and the solid discharged under an atmosphere of carbon dioxide. Chemical analysis of the product indicated its nitrogen content to be 2.1 percent (calculated value for Ni_3N, 7.8%).

NLA-6 - The reactor was charged with 10 g of reduced Raney nickel and 1180 psig of N_2 at room temperature. The bomb was then heated with an electrical tape, wound externally, to a temperature of 300°-320° C for a total of 28 hours. On cooling, the nitrogen was bled out and the solid discharged under an inert atmosphere. The material on analysis showed a nitrogen content of 0.03%.

NLA-7 - The charge consisted of 10 g of reduced Raney nickel, an excess of liquid NH_3 and 125 psig N_2. The bomb was maintained at about 135°C for 13 hours (pressure: 2100-2300 psig). The discharged solid had a nitrogen content of 0.4%.

NLA-8 - Charge, 10 g reduced Raney Ni, gaseous NH_3 and 300 psig N_2. Heated at 250°C for 13.5 hours. Pressure 1470-1500 psig. Nitrogen content of the product 0.5%.

As the results in nitriding Raney nickel with pressurized ammonia have not been promising, further work in this area will be abandoned.

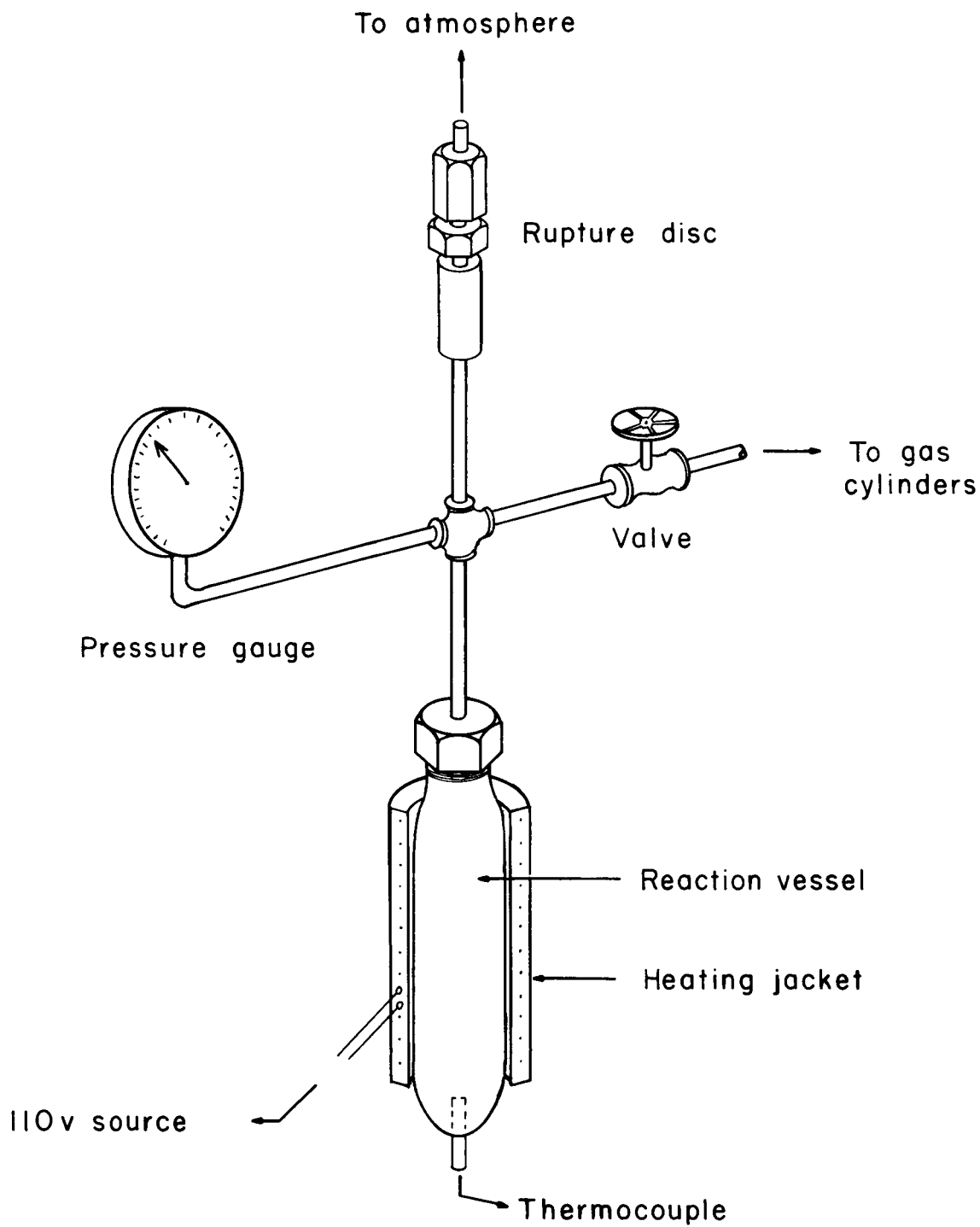*The letters NLA signify "Nickel-Liquid Ammonia studies".

To atmosphere

Rupture disc

To gas
cylinders

Valve

Pressure gauge

Reaction vessel

Heating jacket

110v source

Thermocouple

Figure 1 – Apparatus for reacting reduced metals with pressurized
ammonia

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H. Preparations Based on Raney Alloys

At the suggestion of Tyco Laboratories work with Raney alloys has been discontinued. The small surface area and the poor wetting quality of the Raney preparation made it unattractive as an electrode. The preparations listed in tables 4, 5 and 6 consist of Raney based alloys completed early in the quarter. Procedures for preparing Raney alloys and their subsequent processing and conversion to carbides and nitro-carbides were the same as described earlier (21).

TABLE 4.- <u>Alloys of transition metals</u>
<u>prepared by the Raney method</u>

Mesh size: 150-400

Raney alloy no.	Composition of the leached alloy
RA-19	1Fe-1Au-1Pd
RA-20	1Co-1Au-1Pd
RA-21	1Ni-1Ag-1Pd

TABLE 5.- <u>Preparation of carbides</u> ·

Space velocity of CO: 100 hr^{-1}

Run no.	Charge	Duration of carbiding, hrs	Temp, °C
45C	1Co-1Ag-1Au	4	160-250
		104	250
46C	3Ni-1Ag	6	160-250
		101	250
55C	1Ni-1Pd	4	160-250
		106	250

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TABLE 6.- Preparation of nitrocarbides

Temperature: 260°C
Space velocity of NH3: 1000 hr^{-1}

Run no.	Charge	Duration of nitriding, hrs
31NC	Carbided 1Ni-1Ag	48
32NC	Carbided 3Ni-1Ag	48
33NC	Carbided 1Co-1Ag-1Au	48

I. X-ray Diffraction Study of Transition Metal Alloys

This present diffraction study is a continuation of the one reported in the last quarterly (21). In particular, it is a continuation of our study on the Al-Ni-Co system before and after the leaching of aluminum.

Raynor and Pfeil reported that the aluminum-rich region of the Al-Ni-Co system consists of a primary solid solution (α), Co_2Al_9, and $NiAl_3$. They found that the ($\alpha + NiAl_3$) field was restricted, but that the ($\alpha + Co_2Al_9$) field was very wide, indicating a large solubility of Ni in this compound. The replacement of cobalt by nickel proceeds atom for atom up to a limit represented by the composition--cobalt 10.28, nickel 22.90, aluminum 66.82 percent (22).

A more detailed study of the ternary was felt necessary, since one can logically assume no structural rearrangement during the leaching and reduction of the ternary melts of Raney Ni and Raney Co. The structure of the leached and reduced melts should be dependent on the phase or phases present in the ternary melt; the only change in crystal structure being caused by the removal of Al from its lattice positions.

The first step in this study was re-examining in detail Raney Ni and Raney Co. The phase diagram of the Al-Ni system (23) showed that at 42 ± 5% Ni by weight there was primarily $NiAl_3$ with some Ni_2Al_3. Our x-ray analysis verified this. The Al-Co phase diagram showed, at 40 ± 5% cobalt by weight, the possible presence of Co_2Al_9, Co_4Al_{13}, and Co_2Al_5; x-ray analysis verified the presence of Co_2Al_9 and Co_2Al_5.

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It was decided to recreate the Al-Ni-Co system by melting appropriate amounts of Co_2Al_9 and $NiAl_3$, the thought being that these two aluminum compounds might form a pseudobinary system as does $MgCu_2$-$MgNi_2$ (24). These melts were prepared in Ni/Co ratios of 1.00, 0.33, and 3.00 (see table 7). A simple etching procedure confirmed the presence of $NiAl_3$ and Co_2Al_9 phases in all three of our melts. The first melt, which was cooled slowly under a helium atmosphere, showed crystal growth on its surface. These crystals under microscopic analysis proved to be the needle-like crystals of $NiAl_3$ and the plate-like crystal of Co_2Al_9. X-ray diffraction analyses have not as yet been completed.

It is a good assumption to say that the Raney nickel-Raney cobalt, $NiAl_3$-Co_2Al_9 and the Al-Ni-Co systems are the same. In the previous quarterly report (21) we reported the presence of a new distinct species; it appears now to be the primary solid solution mentioned by Raynor and Pfeil. RA-1 was re-examined and was shown to have Co_2Al_9, $NiAl_3$, and a series of lines which we account to the solid solution. Now if Co_2Al_9 and/or $NiAl_3$ were the predominant phases one would expect the leached-reduced Raney Ni-Raney Co to be free Ni and free Co; but as was reported earlier there is no free Ni or free Co present. As nickel is soluble in Co_2Al_9, a monoclinic crystal (25), we can eliminate this as a possibility as far as our main phase is concerned as we exceeded the limiting bounds of nickel's solubility. $NiAl_3$ is completely eliminated because of cobalt's restricted solubility in it.

We may conclude that the primary solid solution phase which would be a face-centered cubic structure is the cause of the phenomena we are observing in the RAL series. Why upon removal of the aluminum we are still left with the face-centered structures is still a question to be answered.

The lattice parameters for RAL-1 and 1Ni-1Co alloy have been re-calculated along with those of RAL-2, RAL-3, and 3Ni-1Co (see table 7). The series of leached and reduced Raney melts shows an increase in lattice parameters with an increase in cobalt content. Quantitative data are still being done for the Raney Ni-Raney Co reduced and leached melt (Ni/Co = 0.25 by weight) but from all indications it should fit consistently with the above conclusion. It is interesting to note that the hexagonal phase has finally appeared faintly in this melt. It would seem that we are finally reaching the limiting point of the cubic structure at around 80 percent cobalt.

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TABLE 7.- Crystal structures of Ni-Co preparations

Sample no.	Composition, weight-percent			Treatments		Lattice parameters	Crystal structure
	Ni	Co	Al	Number of leachings	Number of reductions		
RAL-1	43.5	54.5	2.00	2	1	a = 3.546 Å	f.c. cubic
RAL-2	22.8	75.6	1.55	2	1	a = 3.557 Å	f.c. cubic
RAL-3	72.5	25.0	2.35	2	1	a = 3.539 Å	f.c. cubic
RAL-4				2	1	a = 3.561 Å	f.c. cubic, faint hexagonal
1Ni-1Co alloy	50.01	49.99	trace			a = 3.534 Å	f.c. cubic
1Ni-3Co alloy	25.01	74.99	trace				hexagonal
3Ni-1Co alloy	74.99	25.01	trace			a = 3.532 Å	f.c. cubic
4Co-1Ni alloy	80.00	20.00	trace				hexagonal
NiAl3	42.02	trace	57.98				orthorhombic
Co2Al9	trace	32.68	67.32				monoclinic

A statistical treatment has been applied and shows that the inter-planar spacings are accurate to 1 part in 200, lattice parameters to 1 part in 350, and the relative intensities (21) have a 10 percent uncertainty due to the inherent electrical noise of the densitometer and the strip recorder.

Conclusion

It would seem that the primary solid solution of Al-Ni-Co$_9$, which in itself has the face-centered cubic crystal structure, is the only phase which could possibly be the determining factor affecting the structure of the leached ternary melt. The intricate lattice effects and structure that allow the material to remain in a face-centered cubic structure still remain a mystery. We have shown that the reduced and leached Raney Ni-Raney Co system is in a face-centered cubic structure up to approximately 80 percent cobalt, at which point there is an appearance of the hexagonal close-packed structure along with the cubic structure. This is at least qualitatively analogous to the binary Ni-Co system in which the hexagonal structure coexists with the cubic structure above 70 percent cobalt (26). Both systems may not be the same but both are examples of primary solid solutions of nickel and cobalt. Both show one primary phase throughout their regions which is the same structure as one of their initial components, in this case Ni, and both show expanding lattices with increase in cobalt content.

Work Plan

During the next quarter the preparation of coprecipitated hydroxides of binary and ternary combinations of transition metals, in different proportions, will be continued. These hydroxides will be reduced, carbided and nitrocarbided. Borides of the transition metals, singly and in combination, will be prepared.

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APPENDIX I

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Samples shipped to Tyco Laboratories to date -------------- 121

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