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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE
IN ALKALINE H₂-O₂ FUEL CELLS

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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE
IN ALKALINE H₂-O₂ FUEL CELLS

The objective of this project is the synthesis of interstitial compounds for increasing the efficiency of the oxygen electrode in alkaline H₂-O₂ 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 D. Bienstock, Sayeed Akhtar, and C.T. Grein.

Bureau of Mines
Pittsburgh Coal Research Center

Quarterly Report for the period ending December 31, 1966

Development of An Improved Oxygen Electrode for Use in
Alkaline H₂-O₂ Fuel Cells

Summary

Preparations of epsilon, chi, and theta-iron nitrocarbides, and epsilon- and gamma-iron carbonitrides were synthesized and shipped to Tyco Laboratories, Inc. In addition, the following compounds have been prepared and are ready for shipment:

(a) Chi-iron carbides and the corresponding nitrocarbides from coprecipitated mixtures of iron and silver in the weight ratios of 3/1, 1/1, and 1/3 iron to silver.

(b) Carbides of cobalt and nickel.

Attempts at preparing the nitrides of cobalt and nickel were unsuccessful.

The induction furnace is now in operation and three Raney alloys of Co-Ni in the weight ratios of 3/1, 1/1, and 1/3, and one Raney alloy of 1Ni-3Ag have been prepared. The Raney Co-Ni alloys have been leached and the activated materials are under treatment for conversion to carbides.

Introduction

The objective of this project is to develop catalysts for the cathodic reduction of oxygen in alkaline H₂-O₂ fuel cells. The work is being conducted in cooperation with Tyco Laboratories, Inc., and the materials under investigation are the interstitial compounds of the transition elements iron, cobalt, and nickel, with carbon, nitrogen, boron, and silicon. This report deals only with the preparation of these compounds; information on the cathodic efficiency of the preparations in laboratory-scale tests may be obtained from the Quarterly reports of Tyco Laboratories.

In the work plan proposed in the first Quarterly Report, a list of 79 groups of compounds was suggested as of potential interest in connection with this work. Later, in consultation with the Tyco Laboratories, a priority list of 26 selected groups was arrived at. Preparation of the carbides, nitrides, nitrocarbides and carbonitrides of iron and of the coprecipitated mixtures of iron and silver is now complete, and our efforts are now directed at the preparation of the compounds in the priority list which consists of the carbides, nitrides, nitrocarbides and carbonitrides of nickel and cobalt and of the alloys of these metals with each other and with silver and gold.

Experimental Procedure

The apparatus and techniques have been described in the First Quarterly Report (1). All chemicals and gases used were of commercial grade. Products were identified by the x-ray diffraction patterns supplemented by chemical analysis.

A. Compounds of Iron

Nitrocarbides - These were prepared from carbides of iron, the preparation of which has been described (1).

A known weight of iron carbide was transferred to the Vycor reactor tube under a strong flow of CO₂. After transfer, N₂ was used to flush the CO₂. A flow of NH₃ was then started and the temperature raised to the desired level and maintained for the duration of the nitriding. When the reaction was completed and on reaching room temperature the catalyst was transferred from the Vycor nitriding vessel under a strong flow of N₂ into a collection flask. The collection flask was then placed in a nitrogen-filled dry box and samples taken for x-ray diffraction and chemical analysis. Conditions for nitrocarbiding are shown in table 1.

Upon nitriding χ -Fe₂C with ammonia, nitrogen replaces carbon in the carbide lattice producing chi iron nitrocarbide. When sufficient nitrogen is added to induce instability in the chi structure, transformation to the epsilon iron nitride occurs. As shown in table 1 under mild nitriding conditions, 280°C and 15 hours, χ -Fe₂C was converted to χ -Fe₂X(C,N) in run 6NC. Whereas in run 4NC, nitriding at 350°C for 20 hours, the chi was transformed to epsilon iron nitrocarbide. A similar reaction occurs with theta Fe₂C. Under mild nitriding, 6 hours at 300°C, the theta iron nitrocarbide was obtained in runs 5NC and 7NC. Whereas in 3NC (1) nitriding at 350°C for 24 hours transformed the theta to the epsilon nitrocarbide. Runs 4NC, 6NC, and 7NC were prepared from a leached Raney iron. Run 5NC was prepared from an alkali-promoted magnetite.

TABLE 1.- Nitriding of iron carbides

Run No.	Charge	Charge wt., g.	X-ray analysis	Gas	Hourly space velocity, hr. ⁻¹	Average bed temp., °C	Duration of nitriding, hrs.	Discharge, wt., g.	X-ray analysis	Chemical analysis, wt.-%		
										Total C	Free C	Nitrogen
4NC	5C	34.5	X-Fe ₂ C, α-Fe	NH ₃	1000	350	20	35.3	ε-Fe ₂ X(C,N)	3.84	1.09	6.64
5NC	14C	35.1	θ-Fe ₃ C	NH ₃	1000	294	6	35.0	θ-Fe ₃ X(C,N)	8.13	3.53	0.78
6NC	7C	15.0	X-Fe ₂ C	NH ₃	1000	280	15	14.7	X-Fe ₂ X(C,N)	7.35	6.0	1.13
7NC	15C	29.9	θ-Fe ₃ C	NH ₃	1000	300	6	29.8	θ-Fe ₃ X(C,N)			
8NC	21C	13.0	Ag, X-Fe ₂ C	NH ₃	1000	280	19	13	Ag, X-Fe ₂ (C,N)			
9NC	22C	15.0	Ag, X-Fe ₂ C	NH ₃	1000	280	15	14.9	Ag, X-Fe ₂ (C,N)			
10NC	24C	15.0	Ag	NH ₃	1000	280	15	14.9	Ag			0.37 ^{a/}

a/ Fe 25.0%.

Carbonitrides - The starting materials for these preparations were iron nitrides, the preparative methods for which have been described (1).

A known weight of iron nitride was transferred to the Vycor reaction tube under a strong flow of N_2 . To avoid stripping the nitrogen in the nitride pure CO was substituted for the $10H_2+1CO$ mixture. The CO, flowing through an activated carbon trap, was passed through the nitride at an hourly space velocity of 100. The temperature was set to the desired level on the temperature controller and the gas effluent monitored by the infrared or thermal conductivity unit. Upon completion of the reaction the reactor was quickly cooled under a CO flow. When room temperature was reached the catalyst was transferred from the Vycor carbiding vessel to the collection flask. The collection flask was placed in the inert box, samples were taken for x-ray and chemical analysis. Conditions for carbonitriding are shown in table 2.

Carbiding iron nitride with carbon monoxide at $350^\circ C$, converts the epsilon, gamma, and zeta nitrides to epsilon iron carbonitride. Carbiding at milder conditions, $250^\circ C$ for 4 hours, converts the gamma nitride to gamma iron carbonitride. Runs 6CN, 7CN, and 8CN were prepared from a coprecipitated Fe-Ag mixture containing 3/1, 1/1, and 1/3 weight ratios of Fe/Ag. Run 9CN was prepared from an alkali-promoted magnetite, and 10CN from leached Raney iron.

B. Compounds from Coprecipitated Iron-Silver Oxides

Carbides - Coprecipitated iron and silver oxides, to give a weight ratio of Fe/Ag of 3, 1, and 0.33, were prepared by treating the mixed metal nitrates with Na_2CO_3 , washed with water, and dried at $110^\circ C$. The oxides were reduced with hydrogen at $450^\circ C$. The $\chi-Fe_2C$ phase was obtained by carbiding with carbon monoxide at an hourly space velocity of 100, for 45 hours at a stepwise progression from 170° to $350^\circ C$. X-ray diffraction showed, in addition to the strong Ag lines, faint lines of $\chi-Fe_2C$ for the 1Fe/1Ag mixture with no evidence of its presence in the 1Fe/3Ag mixture. As the strong lines of $\alpha-Fe$ are not present in the 1:3 mixture and as chemical analysis shows 25 percent Fe this would indicate that the carbide which was produced was of very small crystallite size. The details of the preparation are given in tables 3 and 4.

TABLE 2.- Carbiding of iron nitrides

Run No.	Charge	Charge wt.,g.	X-ray analysis	Gas	Hourly space velocity hr. ⁻¹	Bed temp., °C	Duration of carbiding, hrs.	Discharge wt.,g.	X-ray analysis	Chemical analysis, wt.-%	
										Total C	Free C
6CN	11N	30.4	ϵ -Fe ₃ N, Ag	CO	100	225-350(319) 350	3 7	30.4	ϵ -Fe ₂ X(C,N), Ag		
7CN	15N	37.6	ϵ -Fe ₃ N, Ag	CO	100	185-350(306) 350	5 5	37.6	ϵ -Fe ₂ X(C,N), Ag		
8CN	16N	37.6	Ag, ϵ -Fe ₃ N	CO	100	202-350(305) 350	4 6	37.2	Ag, ϵ -Fe ₂ X(C,N)		
9CN	21N	40.1	γ' -Fe ₄ N, ϵ -Fe ₃ N	CO	100	200-250(243) 250	$\frac{1}{2}$ 3 $\frac{1}{2}$	40.1	γ' -Fe ₄ X(C,N)		
10CN	8N	17.7	γ' -Fe ₄ N, ζ -Fe ₂ N	CO	100	200-250(223) 250	1 3	17.1	γ' -Fe ₄ X(C,N)		

a/ First figure is temperature at which reaction started, second figure is maximum temperature of carbiding, third figure is the average temperature of carbiding.

TABLE 3. - Coprecipitation of mixed oxides of iron and silver

Run No.	Reactants other than H ₂ O, g.					Dried discharge wt., g.	Fe/Ag wt. ratio
	Fe(NO ₃) ₃ ·9H ₂ O	AgNO ₃	Na ₂ CO ₃	H ₂ O	Other		
38CP	139.86	10.14	Na ₂ CO ₃	450	35.95	3/1	
39CP	do	26.79	do	450	44.41	1/1	
40CP	do	59.25	do	450	59.61	1/3	

TABLE 4.- Pretreatment and carburizing

Run No.	Pretreatment					Carburization						
	Charge	Charge wt., g.	Hourly space velocity, hr. ⁻¹	Temp., °C.	Time, hr.	Gas	Hourly space velocity, hr. ⁻¹	Temperature, °C.		Time, hr.	Discharge, wt., g.	X-ray diffraction
								Front of bed	Rear of bed			
21C	38CP	33.95	2500	443	14	CO	100	170-357	157-329	45	27	Ag, X-Fe ₂ C
22C	39CP	42.41	2500	446	11	CO	100	170-350	167-343	45	36	Ag, X-Fe ₂ C
24C	40CP	57.61	2500	452	13	CO	100	170-350	151-329	45	49	Ag
17C	Leached Raney nickel	44.78				CO	100	160-249(232)	155-244(229)	7	46.1	Ni ₃ C, Ni trace
		42.80				CO	100	250	228	24	43.8	Ni ₃ C, Ni trace
		43.2				CO	100	300	257	24	49.8	Ni ₃ C, Ni trace
18C	Leached Raney cobalt	40.54				CO	100	200-300	185-297	22	47.2	Co ₂ C, Co
								300	297	49		
19C	Leached Raney nickel	53.19				CO	100	180-250	161-236	29	55.2	Ni ₃ C, Ni
		54.33				CO	100	250	236	48	55.2	Ni ₃ C, Ni trace
								251	233	20		
20C	Leached Raney cobalt	49.95				CO	100	180-250	167-240	4	51.0	Co ₂ C, Co
		50.41				CO	100	250	240	48	50.1	Co ₂ C, Co
								260	241	27		

Nitrocarbides - The carbides were nitrated with ammonia at 280°C for 15 hours. The χ -Fe₂(C,N) lines in x-ray diffraction were again faint with the 3Fe/1Ag, and the 1Fe/1Ag preparations (Runs 8NC and 9NC) and were not evident on the 1Fe/3Ag preparation (10NC). The details of these preparations are shown in table 1.

C. Compounds of Nickel and Cobalt

Compared to iron, nickel and cobalt appear to offer far less diversity in forming carbides and nitrides, the generally accepted stoichiometric combinations being Ni₃C and Ni₃N for nickel and Co₂C and Co₂N for cobalt.

Carbides - The formation of Ni₃C by the action of CO on reduced Ni was investigated by Bahr and Bahr (2) and more recently, by Eyraud (3) and his coworkers. Their results, which are in substantial agreement, are represented in figure 1. Below 250°C, the reaction proceeds very slowly. However, at temperatures higher than 285°C, carbide formation is accompanied by deposition of free carbon. This is indicated by inordinately large carbon/metal ratios, far in excess of that for Ni₃C. Further, the combined carbon can be distinguished chemically from the 'free' carbon; the former reacts with H₂ at about 200°C (180°C, according to Bahr and Bahr), whereas the 'free' carbon does not react with H₂ at temperatures below 450°C.

Co₂C has been the subject of extensive studies in view of its possible role as an intermediate in the Fischer-Tropsch synthesis on cobalt catalysts (4). The formation of Co₂C by the action of CO on the elemental metal and its thermal instability is comparable to the corresponding aspects of the chemistry of Ni₃C. Like Ni₃C, Co₂C is reduced by hydrogen at about 200°C.

Preliminary effort was directed at preparing the carbides of nickel and cobalt by a method analogous to that employed for the preparation of the carbides of iron, namely by passing mixtures of carbon monoxide and hydrogen over activated Raney metals at elevated temperatures. However, it was found that as soon as the temperature was raised to about 180°C, Fischer-Tropsch synthesis reaction set in and the temperature of the bed increased rapidly by as much as 200° to 300°C, depending on the composition of the feed gas. Analysis of the exit gas indicated almost quantitative conversion of CO to CH₄. The tendency for the temperature to run away uncontrollably was minimized by recirculating part of the exit gas; however, no carbide formation was indicated when samples of the metals so treated were analyzed by x-ray diffraction. This is in agreement with the earlier observation of Weller, Hofer, and Anderson (5) that no detectable amount of the carbide of cobalt is formed under conditions of Fischer-Tropsch synthesis.

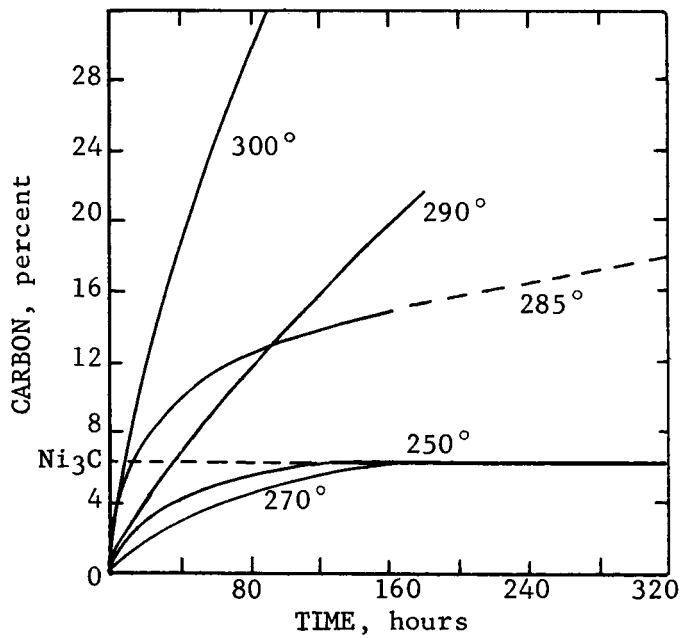
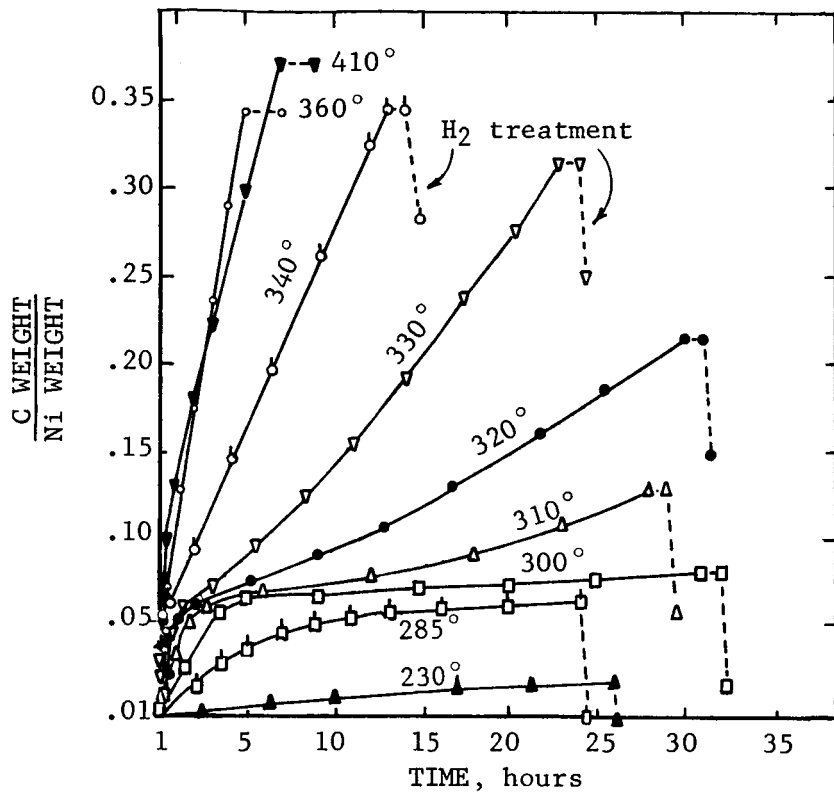


FIGURE 1. - Carburization of Nickel; Upper Figure According to Eyraud (3), Lower Figure According to Bahr and Bahr (2).

Ni_3C was prepared by passing CO on activated Raney nickel at $250^\circ C$ for 48 hours at an hourly space velocity of 100. X-ray analysis of the product so obtained indicated Ni_3C as the major phase, with small amounts of metallic nickel. The material was carbided further, under the same conditions, for an additional 20 hours after which only a trace of metallic nickel was detectable. The preparation has been labelled 19C. A separate sample, 18C, of Raney nickel was treated with CO at $300^\circ C$, but the product so obtained was found to be contaminated with metallic nickel to a greater extent than the one which was obtained by carbiding at $250^\circ C$. The large weight gain is indicative of carbon deposition occurring at the higher temperature (see table 4).

Co_2C was prepared by passing CO on activated Raney cobalt at $250^\circ C$ for 48 hours at a space velocity of 100 hr.^{-1} . X-ray analysis indicated the presence of some metallic cobalt in the preparation which however could not be eliminated even after a continued carbidation for an additional 24 hours at $260^\circ C$. The preparation is labelled 20C. When a separate sample of Raney cobalt, 18C, was carbided with CO at $300^\circ C$, x-ray analysis of the product indicated the presence of a larger residual amount of uncombined cobalt than in the sample 20C. The large weight gain of the higher-temperature preparation is indicative of carbon deposition (see table 4).

Aliquots of 19C and 20C are under processing for the preparation of the nitrocarbides of nickel and cobalt respectively.

Nitrides - The chemical researches of Hagg (6) and of Juza and Sachze (7) on the preparation and properties of Ni_3N have been reviewed by Hofer (4). The formation of this compound by the action of gaseous ammonia on nickel has been re-investigated recently by Rienaecker and Hohl (8). The rate of this reaction is dependent both on the temperature and on the space velocity of ammonia. Ni_3N is known to decompose at temperatures $\geq 360^\circ C$ with measurable rates (7). Accordingly, lower temperatures would favor the yield of Ni_3N , as was found by Rienaecker and Hohl (8) who observed that the percentage conversion of nickel to the nitride decreased as the reaction temperature was raised in the range 175° - $600^\circ C$, the flow rate of ammonia and the duration of nitriding being the same throughout. The significance of the flow rate of ammonia is less clearly understood. However, experimental evidence (8) suggested that the formation of Ni_3N is dependent on a suitable space velocity of the gas, departure from which, on either side, is deleterious to the yield of the nitride. The nitride of cobalt, Co_2N , has also reportedly been prepared by decomposition of the cobalt amide (9). However, the preparation of the cobalt and nickel nitrides appears to be attended by unusual difficulties and the success achieved by various workers differs widely.

A 40-gram charge of activated Raney nickel was treated with NH_3 at an hourly space velocity of 1,000, first at 175°C for 48 hours, then at 300°C for 24 hours, and finally at 380°C for 24 hours. Small samples were withdrawn each time for x-ray analysis which, in all cases, failed to show formation of any nitride. Parallel experiments with Raney cobalt in the temperature range 200°C - 450°C and space velocities $1,000$ - $100,000 \text{ hr.}^{-1}$ of NH_3 were equally fruitless. Some indication of the formation of traces of Co_3N was obtained when cobalt was treated with NH_3 (s.v. $10,000 \text{ hr.}^{-1}$) at 430°C .

As a variation of the above approach, a separate sample of Raney nickel was charged in a pressurized system and the metal was treated with flowing NH_3 (and subsequently with a mixture of NH_3 and N_2) at 380°C - 390°C and a pressure of 75 pounds psig. No trace of nitride was detected in the highly pyrophoric discharged material even after prolonged treatments extending over several days.

The investigation of the nitriding of cobalt and nickel will be continued.

D. Preparation of Co-Ni and Ni-Ag Alloys

Three- and four-component Raney alloys of the type Al-Co-Ni or Al-Co-Ag-Au are not available commercially. These are, therefore, being prepared in the laboratory. The Al component will then be leached out to obtain an activated mixture of the remaining metals.

Three different Raney alloys of Al-Co-Ni have been prepared which on leaching will give mixtures of approximately 75Co-25Ni, 50Co-50Ni, and 25Co-75Ni. The Raney alloys were prepared by melting together appropriately weighed amounts of commercial Al-Ni and Al-Co alloys in an induction furnace, shown in figure 2. The molten mass, on cooling, was crushed to a powder and sieved to 150-200 mesh. The aluminum was leached with caustic soda and thoroughly washed with water.

One Raney alloy of Al-Ni-Ag has been prepared which after removal of Al will yield a mixture of 75Ag-25Ni. It was not possible to crush this Al-Ni-Ag alloy to powder; the material was not friable. Accordingly, the mass was machined into wirelike turnings which were then repeatedly run through a hammer mill. The powder so obtained was passed through a 40 mesh sieve. The Al component was removed, as usual, by treatment with alkali.

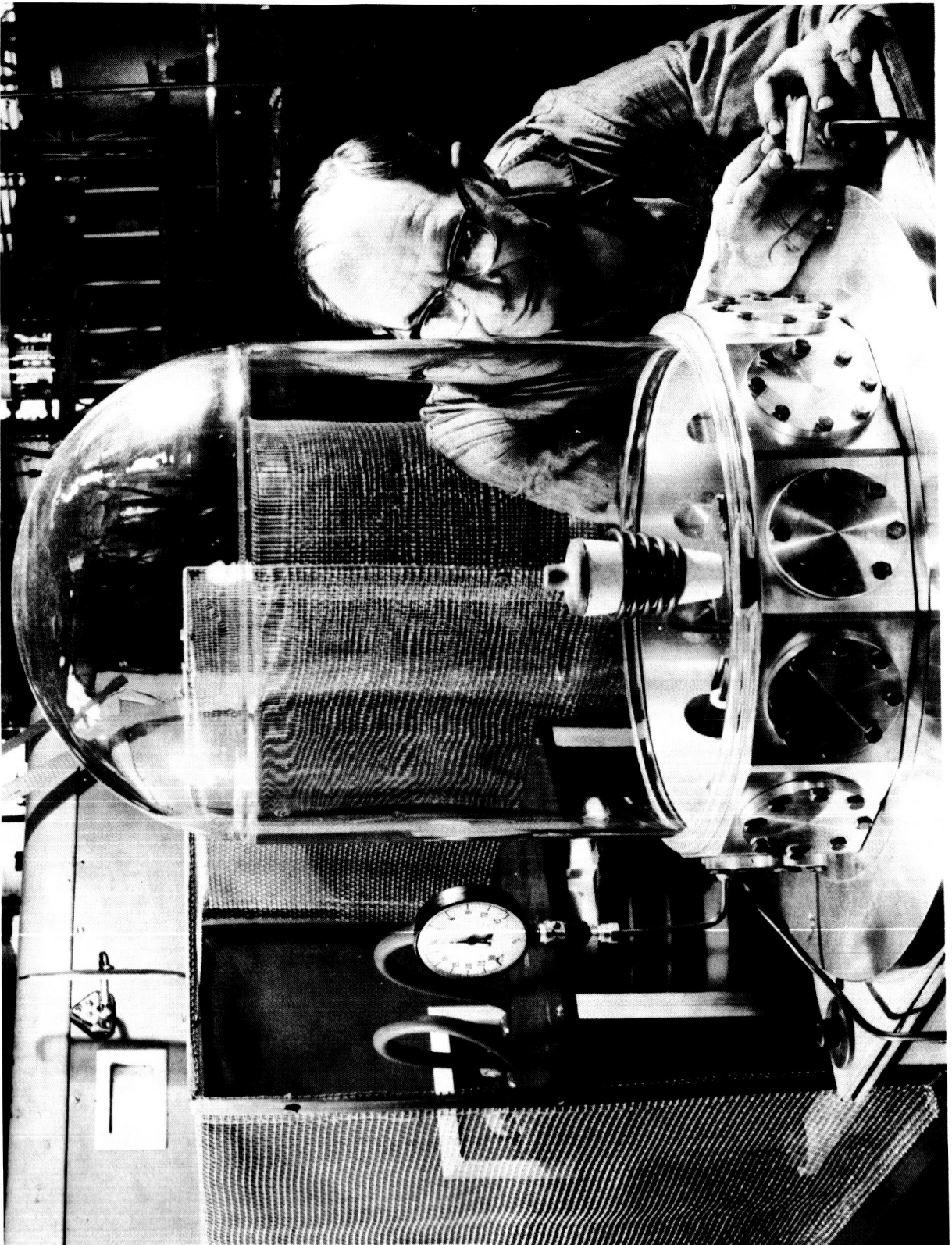


FIGURE 2. - Induction Furnace for Melting Alloys.

Work Plan

During the next quarter preparation of Raney alloys of Ni-Ag, Ni-Au, Co-Ag, Co-Au in 1/1, 3/1, and 1/3 weight ratios, and Ni-Co-Ag and Ni-Co-Au in a 1/1/1 weight ratio will be prepared. The activated mixture will be carbided and nitrocarbided.

The investigation of nitriding nickel and cobalt will be continued. When nitriding is successfully accomplished, the techniques will be applied to the above alloys.

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^{a/} Titles enclosed in parentheses are translations of the original titles.