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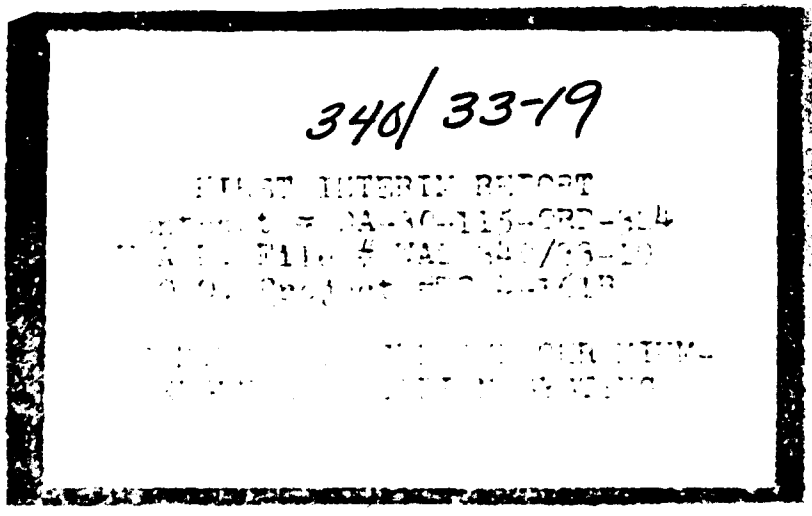

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Rensselaer Polytechnic Institute

DEPARTMENT OF METALLURGICAL ENGINEERING

Troy, New York

FIRST INTERIM REPORT
Contract # DA-30-115-ORD-324
W.A.L. File # WAL 340/33-19
O.O. Project #TB 4-161B

CHROMIUM-NITROGEN AND CHROMIUM-OXYGEN EQUILIBRIUM SYSTEMS

First Interim Report

Contractor: Rensselaer Polytechnic Institute

Agency: Office, Chief of Ordnance, ORDTR-Cannon

Ordnance District: Rochester

Contract Number: DA-30-115-ORD-324

W.A.L. File Number: WAL 340/33-19

O.O. Project Number: TB4-161B

Title of Project: Chromium-Nitrogen and Chromium-Oxygen Equilibrium Systems

Object:

To study the behaviour of pure chromium metal when heated in atmospheres of oxygen and nitrogen and to obtain data to plot a constitution diagram for the chromium-oxygen and chromium-nitrogen system.

Summary:

Apparatus for the preparation of Cr-O alloys below the dissociation pressure of Cr_2O_3 has been improved to the point where a range of compositions can be produced in the single phase α-Cr region of the diagram. A vacuum-fusion analysis system is now being used successfully to analyze these alloys for oxygen. To date sufficient results have been obtained at 1725°F to tentatively fix the solubility limit of oxygen at this temperature at 0.45 to 0.49 wt. %. Further experiments with high oxygen containing

atmospheres indicate that only the oxide Cr_2O_3 is formed. Attempts to experimentally establish the dissociation pressure vs. temperature curve for Cr_2O_3 by means of "bracketting" the temperature at various partial pressures in the dissociation range proved to be time consuming and insensitive. However results indicate that calculated curves published by Lustman are too low.

For the Cr-N system, both ammonia-helium atmospheres and nitrogen-helium atmospheres are being used in conjunction with the micro-Kjehdahl method of analysis to produce isotherms. Two of these at 1652°F (900°C) are sufficiently complete to give information about the constitution diagram. With the NH_3 atmospheres high nitrogen containing alloys are obtained which establish the boundary of the Cr_2N phase at approximately 11% nitrogen by weight at this temperature, which is in keeping with the Stoichiometric ratio. With the nitrogen atmospheres low nitrogen alloys are obtained. Data presented for this isotherm are insufficient to definitely establish a point on the diagram. A high temperature furnace has been constructed enabling studies to be made up to 3000°F.

Coincident with the isotherm studies the effect of time of treatment on approach to equilibrium was studied. These results indicate that practical equilibrium can be approached by appropriate treatment.

Some hardness surveys of nitrided solid specimens are presented to indicate the relative properties of the nitride phases.

Studies of weight changes during nitriding indicate that this method is insensitive as a means of locating phase boundaries.

Conclusions:

1. Chromium dissolves approximately one half of one percent of oxygen by weight at a temperature of 1725°F. (940°C).
2. The oxide Cr_2O_3 is the only intermediate phase on the chromium-oxygen constitution diagram.
3. The Cr_2N phase exhibits low solubility for nitrogen around the stoichiometric ratio.
4. The dissociation pressures of the CrN phase and Cr_2N phases at 900°C appear to be close to each other.
5. Ammonia atmospheres produce high nitrogen content in chromium whereas molecular nitrogen atmospheres produce low nitrogen content.
6. The structure and dimensions of the Cr_2N phase are very similar to those of so-called hexagonal chromium as reported in the literature.
7. Nitriding solid chromium specimens produces a very hard and corrosion resistant case.

Authors:

John N. Ramsey, Henry Hahn and Arthur A. Burr.

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SCOPE OF REPORT

This report covers work done under Contract No. DA-30-115-ORD-324 between the dates July 1, 1952 and December 31, 1952. This is a continuation of work begun under Contract No. DA-30-115-ORD-116.

As there is little correlation between the behaviour of chromium in the two different atmospheres, the procedure of previous reports has been followed in dividing the main portion of the report into two sections as follows:

Part A: The Chromium-Oxygen System

Part B: The Chromium-Nitrogen System

INTRODUCTION

Preliminary work on this problem, which included a survey of literature, construction of apparatus and establishment of techniques was carried out under the previous contract referred to above and is described in the final report on this contract under W.A.L. File No. 340-33-12. For convenience in introducing to the work in this report, brief reference will be made to this material.

As previously indicated, one of the most generally used methods for the determination of metal gas equilibria is the "isotherm method". Since the work described below makes extensive use of this method, it will be briefly reviewed. For purposes of illustration, the chromium-oxygen

system will be used, although the chromium-nitrogen system would serve equally well.

This procedure can best be illustrated by a diagram as in Figure 1. Several equilibrium alloys, formed at a temperature T_1, but at various partial pressures of oxygen less than that necessary to form Cr_2O_3 would, if analyzed for dissolved oxygen, give data which could be plotted as partial pressure oxygen in the gas vs. wgt. % oxygen dissolved in the chromium. The intersection of this curve, which would have to be slightly extrapolated, and the partial pressure of oxygen necessary to form Cr_2O_3 at T_1 would give a point on the solvus curve. Other lines on the equilibrium diagram, if they exist, can be located in a similar manner. The details of using this procedure for each of the two gas systems involved will be described in the appropriate section of the report below.

Part A

The Chromium-Oxygen System

Introduction:

Briefly, the facts from previous work on this system which became the starting point for this report are outlined below.

A literature survey established that Cr_2O_3 was the only oxide to be expected at temperatures greater than

1000°F. This was verified using pure oxygen for temperatures ranging from 1500-2200°F (820-1210°C) for 18 hours.

A transformation of chromium from Body Centered Cubic to a Hexagonal Close Packed structure was found to appear when pure chromium was heated in a hydrogen atmosphere at temperatures greater than 1800°F for long periods. This led to the decision to utilize oxygen from the dissociation of water vapor in an inert gas such as helium instead of using hydrogen atmospheres.

The partial pressure of oxygen at various temperatures due to the dissociation of part of the water vapor in helium of various dew points was calculated, and compared with the conflicting dissociation pressure curves of Cr_2O_3 vs. temperature from the literature. These calculations showed that gas of dew point better than -60°F to -10°F would be required to maintain oxide free chromium from 1600°F to 2100°F respectively.

AIRCO XX welding grade helium was found to have dew points well within this range. However, to maintain this dew point in the furnace and to have a combustion tube of lower dissociation pressure than chromium, it was found to be necessary to use a refractory porcelain instead of quartz reaction chambers, which were found to be porous.

The vacuum fusion method for analyzing oxygen in chromium offered sufficient advantages that apparatus was designed and constructed.

The continuation of this investigation is described in the following pages. This work can be divided into 3 parts:

1. production of oxide-free, low oxygen chromium alloys at varying partial pressures of oxygen along isotherms
2. determination of the dissociation pressure curve of Cr_2O_3
3. chemical and structural analysis of the alloys

Apparatus and Procedure:

1. Helium Distribution System

High grade new rubber and plastic tubing were originally used to transfer the dry helium from the tank to the dew point indicator or to the combustion tube. It was found that rubber is permeable to moisture and that the plastic is extremely difficult to dry out by flushing with dry gas. Glass was utilized on preliminary equipment, and although satisfactory, was discarded in favor of copper tubing. The entire distribution system is now of 1/4" copper tubing with solderless compression fittings. All joints are painted with glyptal, and all needle valves are packed with a low vapor pressure high vacuum grease. All of these precautions were found to be necessary to avoid moisture and oxygen pick-up.

2. Reaction Chambers

Straight McDanel refractory porcelain combustion tubes have been employed in small Kanthal wire wound laboratory tube furnaces to determine the dissociation pressure curve for Cr_2O_3. This is accomplished by utilizing gas of a constant dew point and approaching the unknown temperature of dissociation by "bracketing" from above and below.

Two McDanel refractory porcelain combustion tubes were fitted with Pyrex furnace heads (1), to allow quenching through the furnace atmosphere into a suitable medium. One end of each combustion tube was modified to fit a standard Pyrex Pipe Flange through a gasket.

As refractory porcelain has very low thermal shock properties, it was found necessary to use sheet metal strips to move the alundum boats into the hot zone. In this way, the edges of the strip could heat up very quickly to the temperature of the combustion tube, while supporting the more slowly heating boat. When the boat had reached the temperature of the hot zone, the boat could be safely placed on the tube and the strip removed. Fig. 2 shows schematic sketches of both types of furnaces.

3. Dew Point Controller

It was found that there was insufficient helium in one tank to allow "bracketing" of the dissociation temperature at the fixed dew point of the tank. Therefore it was necessary to have a means of obtaining a series of fixed dew points ranging from about 0°F to -60°F. A controller was designed and built to allow for humidification of helium as it was drawn from the tank and its subsequent refrigeration at a constant temperature to give helium with a known constant dew point. For example, if gas of dew point -20°F was required, and the tanks of helium to be used had dew points ranging from -40 to -125°F, it would be necessary to add moisture, raising the dew point to about -10°F, then refrigerate at -20°F to freeze out the extra water.

The trap consists of 8 feet of 1/4" copper tubing in a methanol bath cooled by a refrigerator unit whose temperature is controlled by a pressure regulator on the vacuum side of the compressor. This control is accurate to ± 0.5°F.

Figure 3 shows the dew point controller and the helium distribution system. It can be seen that the by-pass around the refrigerator coil allows for checking the humidifier operation. All glass-metal seals are made with deKhotinsky cement.

4. Vacuum Fusion Apparatus

The vacuum fusion apparatus has been modified slightly, and its range extended. The present apparatus is sketched in Fig. 4, and photographed in Fig. 5.

A complete procedure has evolved and several determinations of dissolved oxygen in chromium have been made, as well as checks on N.B.S. Standard Steels. This procedure is described below.

(a) Specimen Preparation

Solid specimens are prepared by the method described by Alexander, Murray and Ashley (2).

Sintered oxide-free, low oxygen-chromium alloys are prepared by removing the thin oxide layer, which always forms as the alloy cools across the Cr_2O_3 dissociation pressure curve, and rinsing in acetone.

As chromium is not ferromagnetic, it is necessary to move it around inside the loading arm by means of iron plugs and magnets. The friability of the sintered chromium alloys lead to the use of soldered sheet iron boats. The boats are weighed,

chromium-oxygen alloys specimen placed inside, and the assembly is reweighed. These are then manipulated in the loading arm and emptied into the crucible by magnets. After analysis, the boat can be reweighed, and the total weight of alloy actually dropped into the crucible can be calculated.

(b) Crucible Preparation

The crucible design and quartz thimble loading is according to Guldner and Beach (3).

(c) Degassing

After the quartz thimble is hung in place, the specimens and a suitable amount of cast iron slugs for a flux bath are loaded in the loading arm. The joints are then sealed with Apiezon wax. Degassing, which is initiated with the mechanical pump, of course, must be done very slowly and carefully in steps of less than 1 cm. Hg, with sufficient time between the steps for the pressure to equalize throughout the system. In this way, the gas adsorbed and trapped in the -200 mesh graphite powder about the graphite crucible can come off without blowing the powder around, and

the pressure differences throughout the system are kept low enough that the velocity of gas transport is insufficient to blow any graphite out of the furnace head and into the system.

When the system vacuum is below the fore pump requirements of the mercury diffusion pumps, the latter can be turned on. When the system has reached its ultimate vacuum of approximately 0.2 micron Hg, heat can be applied to the crucible, following the same precautions on gas evolution as outlined above. A maximum temperature of 4530-4710°F (2500-2600°C) is used for 2-3 hours, being limited by the softening temperature of the Pyrex furnace.

(d) "Blanking" the furnace

After the temperature of the furnace has been cut back to 2820-3090°F (1550-1700°C), five or six 4-5 gram slugs of cast iron are dropped into the crucible and thus melted. Pumping is then continued until the furnace blank reaches 1.5-2 micron-liters/min, as measured in the collection volume, including volume V.

McLeod gauges, and the first throat of pump P_2. The blank gas is analyzed by circulating through the copper oxide furnace and trapping first with dry ice and acetone and then measuring the pressure of the residual gases then trapping with liquid nitrogen. It is also necessary to know the blank from the copper oxide furnace through both types of cold baths.

(e) Specimen Analysis

The system is pumped to about 0.2 micron or better, and S_3 is turned to allow P_1 to pump gas from the furnace into the calibrated volume. Then a boat containing the chromium alloy specimen is maneuvered by magnets to the center tube leading to the crucible, and is turned over to dump the specimen. The gas evolved is collected for 15 minutes, and the pressure read on the McLeod gauge. During the gas collection, the dry ice and acetone mixture is placed on the trap. The collected gas is then circulated through the copper oxide furnace at 550°F and the trap by P_2 for 10 minutes. The

pressure of the remaining gas, collected again in the volume, is measured and the process repeated with liquid nitrogen around the trap.

From the four measured pressures, and the previously measured blank rates and analysis, weight of the specimen, temperature of the volume, and the volume itself, it is possible to calculate the weight % hydrogen, oxygen, and either nitrogen (in the steels) or helium (in the chromium-oxygen alloys).

Results and Discussion:

1. Isotherm Alloys

Alloys for several isotherms are being made but, to date, only those for an isotherm at 1725°F (941°C) have been analyzed. The data on these alloys are listed in Table I below:

TABLE I

ISOTHERM AT 1725°F

Alloy No.	Dew Point °F	Wt.% O_2 in Alloy
90-0	-57	0.44
60-0	-62	0.44, 0.48
74-0	-81	0.42, 0.46

Depending on which dissociation curve for Cr_2O_3 is used from the literature (Gulbransen-43°F, Grube and Flad-50°F), these lead to a tentative point on the solvus curve of 0.45 to 0.49 wt. % oxygen dissolved in chromium at 1725°F.

2. Dissociation Pressure

Using 2 tanks of He which, as received had dew points of -62, and -81°F, 17 runs were made in attempts to "bracket" the temperature at which dissociation took place in this atmosphere. The results of this work indicate that the procedure being used is not satisfactory for the following reasons:

(a) It is a time consuming operation for the small amount of data obtained.

(b) The rate of oxidation is very rapid once it begins, making a "disappearing phase" X-ray method practically useless.

(c) The only method of determining whether no oxide has formed is visual and therefore uncertain.

(d) As a result of b and c, results are on the low side.

On the basis of this work, however, it is apparent that the theoretical curve of Lustman is low.

3. Chemical and Structure Analysis

Results of chemical analysis are included in results of 1 above. It is also noteworthy that analyses of N.B.S. Steels by the vacuum fusion apparatus are within acceptable limits.

In addition to the use of X-ray methods for phase detection, some measurements of lattice parameter of alloys made below the dissociation pressure of Cr_2O_3 were attempted to see if any variation existed with varying oxygen content. Measurements were made on the (211) reflection of the B.C.C. structure for alloys prepared at 1775°F (968°C) as follows:

TABLE II

Sample Number	Dew Point °F
73-0	-81
61-0	-62
83-0	mixture of chromium and Cr_2O_3 to get oxygen solubility maximum

No measurable changes were detected.

4. Higher Oxygen Phases

As the CrO_3 has been listed in the literature by Givaudon et al[5] as being produced from Cr_2O_3 at 970°F (520°C), several attempts were

made to duplicate this without success. Both chromium and Cr_2O_3 were treated from 950°F to 1220°F for 18-60 hours in both air and oxygen. All products were Cr_2O_3. It is of interest to note that several color modifications of Cr_2O_3. blue, purple and brown as well as green have been observed. All have the same basic crystalline structure, as shown by X-ray diffraction.

Part B

The Chromium-Nitrogen System

Introduction:

As with the chromium-oxygen system, work to be reported below is based on preliminary studies under the previous contract. This work led to adoption of a suitable nitriding procedure for chromium metal and to a reproducible method for chemical analysis of samples of low and medium nitrogen content. Difficulty was encountered in dissolving samples for analysis containing the higher nitride (CrN). Both the hexagonal Cr_2N phase and the CrN phase were properly identified and the X-ray powder pattern lines properly indexed. The latter were found to be in complete agreement with those given by Blix[6] and Ericson.[7]

The theoretical concepts involved in nitriding of chromium have been discussed in previous reports. It may be of interest to review them briefly here as they affect the

present work. Both ammonia gas and pure nitrogen have been used as the nitriding agent. The chemical equations involved are

$$2\ NH_3 = N_2 + 3H_2 \qquad (1)$$

for which, at any temperature T,

$$K_1 = \frac{(p_{H_2})^3\ (p_{N_2})}{(p_{NH_3})} \qquad (2)$$

and/or

$$N_2 \longrightarrow 2N\ (\text{in Cr}) \qquad (3)$$

for which

$$K_2 = \frac{a^2\ (\text{N in Cr})}{p_{N_2}} \qquad (4)$$

where a is the activity of nitrogen in solid solution in chromium metal.

Since the K's are a function of temperature only, it becomes obvious that for experiments where the NH_3 or N_2 are diluted with an inert carrier gas, either p_{NH_3} or p_{N_2} may be plotted in making the isotherm, where these pressures represent the partial pressures of the gases as used. Where hydrogen is used as a carrier gas, a small change in the equilibrium will result in the case of ammonia. This will, in general, not be a large enough effect to change the shape of a given isotherm.

Apparatus:

The preparation of nitrided samples has been carried out in three furnaces.

Two of these are Kanthal wound tube furnaces, which, traveling on an overhead rail, may be removed rapidly from the stationary reaction chamber, thus permitting rapid furnace cooling. Each furnace is equipped with two thermocouples; one in the winding, and one in the reaction chamber. One of the two low temperature furnaces has a Pt - Pt 10% Rh thermocouple that activates the temperature controller* and a chromel-alumel thermocouple inside the reaction chamber for measurement. On the other furnace, both thermocouples are chromel-alumel. One reaction tube in use at present is made of quartz, the other of McDanel refractory porcelain. A complete description of this apparatus may be found in previous reports. The set-up has been modified to permit simultaneous use of three gases. The drying train has been eliminated, having been found unnecessary in varied ammonia and nitrogen with helium carrier. A schematic sketch of the present apparatus may be found in the appendix of the present report.

The high temperature furnace, which is a recent addition, has been designed to operate at temperatures in

* See last report.

the vicinity of 3000°F. with a power consumption of approximately 12 kw. The reaction chamber is a "McDanel Zircotube", having properties similar to the McDanel tubes described in the first part of the present report, except for better thermal shock resistance. The furnace is heated by non-metallic heating elements, manufactured by the Carborundum Company under the trade name "Globar". The furnace contains four 36" Globars, and is constructed entirely of high temperature Alumina and insulating fire brick. The furnace atmosphere is supplied and regulated identically to that in the two previously mentioned furnaces. The temperature is controlled by means of a variable resistance. The measurement of temperature has been more difficult at the elevated temperatures reached in this furnace, due to the limitations of the common thermocouples. Hence a Leeds and Northrup Optical pyrometer has been employed, with which temperatures good to approximately 5°F are obtainable. The temperatures were obtained only between runs, due to the lack of peep holes or other means of observing the specimen during runs. The temperature in the oven furnace has been found to fluctuate over about 20°F during a 24 hour period at a temperature of 2800°F.

The gases used in the present experiments are the same as described in our previous report.

Micro-Kjeldahl Analysis

This apparatus has been previously described. The detailed analysis procedure as now used is presented in the appendix.

X-ray Method

The general equipment in use has been previously described. In all instances a Debye-Scherrer camera with a rotating specimen mount has been used. Exposure times of six to eight hours are necessary, using CrK_{α} radiation. An aluminum foil filter has been used with good results to reduce film background.

Experimental Procedure:

1. Preparation of Specimens for Phase Diagram Work

Powder electrolytic chromium with an approximate purity of 99.5% has been used in the preparation of alloys for equilibrium determinations.

About 1/2 to 2 gms of the above powder in an alundum reaction boat is placed in the helium flushed quartz reaction chamber, while the furnace is removed. After flushing for an additional 5 minutes, the active gases, NH_3, H_2, N_2 or a combination of these is turned on. All adjustments are made, and after about 10 minutes, during which time the atmosphere inside the furnace is believed to become constant, the furnace, which is at the desired temperature, is slipped over the reaction chamber. (see Fig. 6) The first temperature reading inside the reaction chamber is taken in 15 minutes, after which time the temperature has reached its final magnitude.

By that time the specimens have already sintered.

After three hours the furnace shell is removed, thus causing the specimens to cool very rapidly. After about 1 minute the active gases are turned off and the reaction chamber once more flushed. The specimen is then removed, re-crushed, and re-treated by repeating the above procedure for another three hours. After another re-crushing the specimen is re-treated for 16 hours and then analyzed by means of the previously mentioned micro-Kjeldahl method, as well as X-ray powder method.

2. Preparati . of Specimens in High Temperature Furnace

One or two grams of electrochrome are placed in an alundum boat, which is pushed into the hot zone of the furnace. The properly adjusted atmosphere is circulated through the furnace at least 1/2 hour after insertion of the sample. Prior to closing the furnace by means of an insulating plug and sealing with litharge, the temperature is taken by means of the previously mentioned optical pyrometer (see Fig. 7).

The time of treatment is 20 hours, which time is believed to be sufficient for equilibrium at the high temperatures. Upon completion of the treatment the specimen is pulled into the cold zone of the furnace, where it cools within about 2 minutes. The specimen is then removed from the boat, and prepared for X-ray and/or Kjeldahl analysis.

3. Preparation of Specimens for Hardness Determinations

Four solid chromium specimens* have been treated at 1832°F. (1000°C) in an atmosphere of 100% NH_3. Since the accurate temperature controllers which are in use at present were not as yet available, the accuracy of the above mentioned temperature may be considered good to only ± 10°F.

The times of treatment were 65, 130, 200 and 280 hours, starting with a new specimen in each instance. All but the 130 hour specimen were slow furnace cooled, the latter receiving a rapid air quench.

Each specimen was mounted and prepared for metallographic observation, and micro-hardness surveys. A number of etching reagents were tried without much success, though the nitrided region is observable in unetched specimens.

The micro-hardness survey, using a Kentron Micro-Hardness Tester was difficult due to the porosity and brittleness of the nitrided case, the heavy load (1000 g) necessary, and the shallow case in the first two samples. Due to the porosity and brittleness, the average hardness value may be lower than the true value. Since the case was extremely shallow in the first specimen, no hardness profile is reported for it.

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* Received through the courtesy of Mr. D. Bloom of M.I.T.

Prior to nitriding, each sample was carefully cleaned and the surface activated with dilute HCl.

4. Determination of the Effect of Time of Treatment

A preliminary study has been made to determine the effect of time on the nitrogen content of a sample treated at 1800°F. in a 100% N_2 atmosphere.

All samples were prepared similary to those prepared directly for isothermal $\%N_2$ or $\%NH_3$ vs. "%N recovered" plots, and the samples received the previously described rapid furnace quench.

5. X-ray Diffraction Studies

Most samples were powdered to approximately 320 mesh in preparation to examination by means of the powder method. X-ray powder patterns for the body-centered cubic Cr, the Cr_2N and CrN as well as Cr_2O_3 were observed as described in a previous report. The relative intensity of the nitride lines served as an indication of the extent of nitriding, the dissociation temperature of the Cr_2N phase, and as a guide in chemical analysis.

The powder specimens were made by extrusion. A chromium target tube at a potential of 40 kv and a current of 18 to 19 ma was used. Exposures of rotating specimens were made for 6 - 8 hours.

6. Weight Change During Nitriding

A small sample of electrolytic Cr was carefully weighed in a platinum reaction boat. The specimen was then treated at 1832°F (1000°C) in an atmosphere of 100% NH_3 for

various periods of time. After each treatment the sample was reweighed and re-treated. After the final treatment the sample was X-rayed to make certain that a complete transformation had taken place. The sample was then analyzed for N by the Micro-Kjeldahl Method. Due to the fact that the transformation was virtually complete, the sample could not be digested completely in preparation for the micro-Kjeldahl analysis. The weight of the sample vs. time of treatment was plotted.

Results:

1. Ammonia-Hydrogen Low Temperature Isotherms

An isotherm at 1652°F (900°C) using mixtures of NH_3 - H_2 was prepared. Nine samples were treated, analyzed in duplicate and the results plotted (see Fig. 8). Though these samples do not represent true equilibrium, since they in all instances contained more than one phase, the break in the curve indicates the approximate dissociation pressure of CrN at 1652°F. X-ray patterns of the series gave evidence of the presence of CrN almost throughout the isotherm. Below is a table showing the %N recovered, and crystal structures encountered.

Though by means of the foregoing isotherm it was impossible to gather information regarding the dissociation pressure or composition of the Cr_2N phase, it appears that the single phase Cr_2N region begins in the vicinity of 11% N

TABLE III

pp NH_3 (atm.)	Wt% N	CrN	Cr_2N	BCC (alpha Cr)
.006		none	some	some
.009	10.56 - 10.77	none	some	some
.010	11.42 - 11.58	?	most	none
.015	8.25 - 8.26	none	most	?
.022		faint	most	none
.032	11.70 - 11.85	faint	most	?
.074	13.40 - 13.44	some	most	none
.150	16.34 - 13.44	some	some	none
.177	19.20 - 21.40	most	some	none

by weight. As there appears to be no evidence of a change in shape between 11 and 21%, it is safe to assume that the solubility of Cr_2N for nitrogen is low.

Simultaneously with the above, another isotherm was made at 1832°F (1000°C). This isotherm consisted of only 5 samples. The work was not pursued further due to the presence of CrN even at extremely low pressures of NH_3.

The table below gives the results of this series.

TABLE IV

pp NH_3 (atm.)	Wt.% Recovered	CrN	Cr_2N	BCC (alpha Cr)
.003	7.11 - 7.10	none	most	some
.015	10.70 - 10.83	?	most	none
.074	13.40 - 13.44	some	most	none
.084	11.44 - 12.92	some	most	none
.177	19.20 - 21.40	most	some	none

The above isotherm will be continued later to give the dissociation pressure and composition of the CrN phase at the isotherm temperature.

2. Nitrogen-Hydrogen Low Temperature Isotherm

Another isotherm was produced at 1652°F (900°C) using N_2 - H_2 atmospheres. As had been determined previously, nitrogen is not a sufficiently severe nitriding medium to yield the higher nitride (CrN), and thus the gas was selected with the intention of getting the dissociation data of the Cr_2N phase. That no CrN is obtained with nitrogen atmospheres was confirmed by the X-ray investigation reported previously, and the fact that samples of this series dissolved with relative ease in dilute sulphuric acid.

Though analytical results are at present incomplete, it is apparent that a relatively large amount of nitrogen (in the neighborhood of 6%) enters the chromium lattice when heating in air. In fact, with atmospheres having even very low partial pressures of nitrogen, this appears to occur.

3. High Temperature Isotherm

A high temperature (2705°F or 1485°C) was made using N_2 - He atmospheres (See Fig. 9). This series, though not yet complete, extends from 100% N_2 to 100% He. Thus far five such samples have been produced.

Upon cooling, the samples are sintered to a much greater extent than those produced at lower temperatures, as could be expected. No oxide film has thus far been

encountered, though the specimens are virtually air cooled.

A sample heated for 20 hours in an atmosphere of helium has a body centered cubic structure, whereas samples treated thus at lower temperature showed at least traces of a hexagonal structure.

Most samples made under partial pressures of N_2 above 10% contained the hexagonal phase. The sample made with 100% N_2 may contain some CrN. Samples produced and plotted thus far are listed in Table V below.

TABLE V

P_{N_2} in atm.	Wt.% N recovered	Structure
0	0.14 - 0.15	BCC
.15	.94 - .97	BCC & HCP
.25	8.0 - 8.3	
.75	9.45 - 10.00	
1.00	12.40 - 12.64	HCP & ? Cubic CrN

4. Hardness Determinations

Hardness profiles of three of the four specimens prepared are presented in Figs. 10, 11, 12. The nitrided case upon the specimen treated for the lowest period of time (65 hours) was too shallow to permit more than one hardness reading. No profile is hence shown. A photomicrograph of the hardness readings as they appeared in the 280 - hour

sample appears as Fig. 13. The specimen appears unetched, and is presented only to show the gradual increase in hardness between the matrix and the case. Under the microscope the nitrided region appears yellow to brown (light), and even though the specimens had a finished surface that had been activated prior to treatment, the case was uneven. The latter was probably due to porosity. A maximum hardness reading of over 2200 knoop was recorded, which is probably the nearest to the true hardness of CrN, since porosity and cracking interfered with most of the readings.

The specimen receiving the most rapid quenching rate exhibited the highest hardness value. The latter was the specimen treated for 130 hours. Each specimen contains at least one intermediate hardness value which probably represents the region of the lower nitride, Cr_2N, though the actual hardness of Cr_2N could best be determined accurately if the solid specimens were treated in a nitrogen atmosphere.

5. Determination of the Weight Increase due to Nitriding

The increase in weight of a specimen treated in an atmosphere of 100% NH_3 at 1000°C has been observed and plotted against time (see Fig. 14).

After numerous such treatments the weight became stable, with a weight increase of 43.2 mg in a sample originally weighing 286.8 mg. Though this increase is

somewhat short of what would correspond to the stoichiometric weight change, X-ray diffraction gave evidence of complete transformation to CrN. The complete transformation was further indicated by the extreme difficulty in dissolving the specimen prior to the micro-Kjeldahl analysis.

The main cause of error was formation of some oxide during cooling of the specimen, and the attack of hydrogen on the Pt reaction boat.

6. Determination of the Effect of Time

Since these samples were successively re-treated without the presence of hydrogen in a nitrogen atmosphere with uncontrolled dew point, some oxide was present in all specimens.

One sample was treated for one hour in an atmosphere of 100% N_2 at a temperature of 1000°C. After part of the sample was removed for analysis, the treatment was continued for one more hour, and finally for 4 hours 15 minutes more. The three analyses of the sample appear in Table VI below.

TABLE VI

Total Time of Treatment in Hours	Analysis Wt.% N
1	2.39 - 2.38
2	3.48 - 3.30
6 1/2	16.60 - 16.38

Another sample was treated for longer periods of time. Though final analytical results are not complete, they at present appear erratic due to the presence of oxide in the samples. They do, however, indicate that the reaction rate is extremely slow after 20 hours of treatment.

General Comments:

Though the isotherms presented are incomplete, a definite break in the curve may be observed which would theoretically indicate the transformation conditions. However, true equilibrium conditions are attained only with difficulty, and more than one phase was found to coexist after treatment under given conditions of atmosphere and temperature. Hence the horizontal plateaus should be displaced to the right, and higher nitrogen contents corresponding to transformations recorded. The data presented hereby must therefore involve the time factor, which in the present case is one of 3 successive re-treatments, the first two lasting 3 hours, and the last lasting 16 hours.

Difficulty has been encountered in correctly identifying the hexagonal phase. In the temperature region near 2000°F., where pure Cr should have a body centered cubic crystal structure, a hexagonal structure has often been observed. This phase may have been Cr_2N which may have formed due to improper flushing of the furnace or a leak if the dissociation pressure of this nitride is very low. It has

also been suggested that the structure may be a hydride of chromium, or even a hexagonal phase of the pure metal.

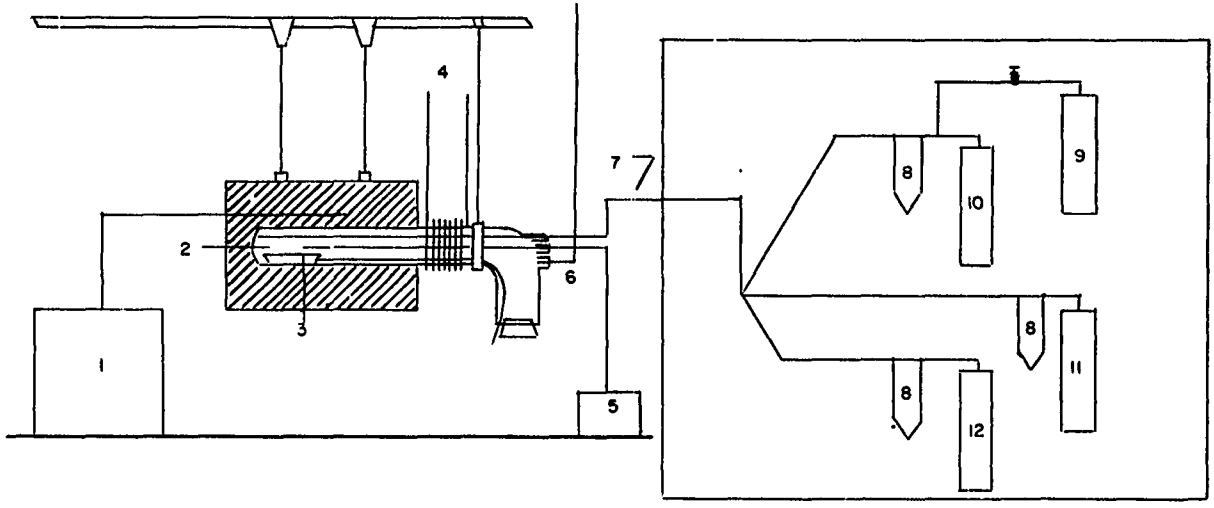
Work under way at present includes a low temperature isotherm using N_2 - H_2 atmospheres at a temperature of about 1450°F. In this temperature range sintering of the specimens is almost absent, hence equilibrium is believed to be more early obtainable.

It has recently been brought to attention that the nitrogen content of the bottled hydrogen in use at this laboratory contains a great enough amount of N_2 as an impurity to yield Cr_2N after prolonged times of treatment. This would explain the presence of the hexagonal phase which could heretofore not be identified.

The nitrogen could be removed from the bottled hydrogen by means of calcium. This will be done in the near future.

APPENDIX I

SCHEMATIC DIAGRAM OF NITRIDING EQUIPMENT



1 AUTOMATIC TEMPERATURE CONTROLLER
2 QUARTZ REACTION CHAMBER
3 SPECIMEN IN ALUNDUM BOAT
4 WATER CIRCULATED COOLING COIL.
5 POTENTIOMETER
6 EXHAUST TUBE
7 INLET

8. MANOMETER
9 AMMONIA.
10. NITROGEN.
11 HYDROGEN.
12 HELIUM.

SCHEMATIC ILLUSTRATION OF LOW TEMPERATURE NITRIDING APPARATUS.

APPENDIX II

APPARATUS AND PROCEDURE FOR NITROGEN DETERMINATION IN CHROMIUM

Apparatus:

A standard micro-Kjeldahl distillation apparatus is used. It is an all Pyrex glass model, with standard taper glass joints and cocks to prevent every possible contamination. The steam generating flask has a capacity of 500 ml. About 70 ml of alkaline solutions can be distilled satisfactorily without loss of sample through splashing past the upper bulbs.

Procedure:

The procedure adapted is a modification of one of Guschbacher's (8) methods.

A 0.1 to 0.2 gram sample is weighed out in a 250 ml Erlemeyer flask, and 20 ml of dilute (1-4) sulfuric acid together with 0.1 gram selenium powder and 5 gm potassium sulphate are added. Digestion is allowed to proceed for two hours, whereupon the sample is centrifuged. The solution is saved, whereas the residue is further treated with a fresh portion of (10 ml) of concentrated sulfuric acid, 5 ml concentrated phosphoric acid, together with 0.1 gm selenium and 5 gm potassium sulfate. Digestion is continued until the solution appears clear. The latter takes from 5 to 10

hours. The combined liquids from both digestions are quantitatively diluted to 100 ml and 25 ml samples distilled over with 10 ml of 40% sodium hydroxide solution. The ammonia is recovered in 25 ml of 0.01 N hydrochloric acid and the excess acid backtitrated with standard 0.01 N sodium hydroxide solution.

A daily blank is obtained in similar manner.

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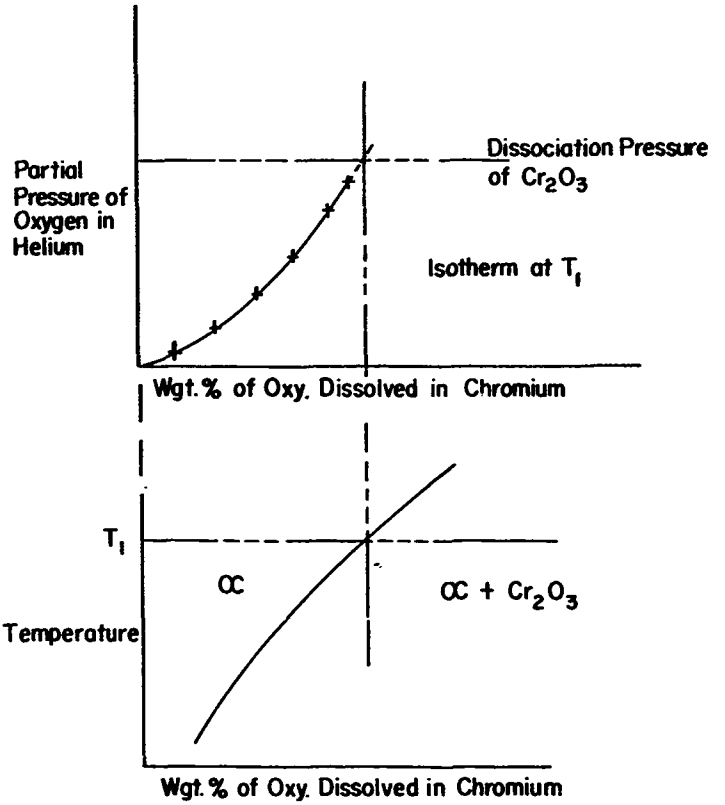
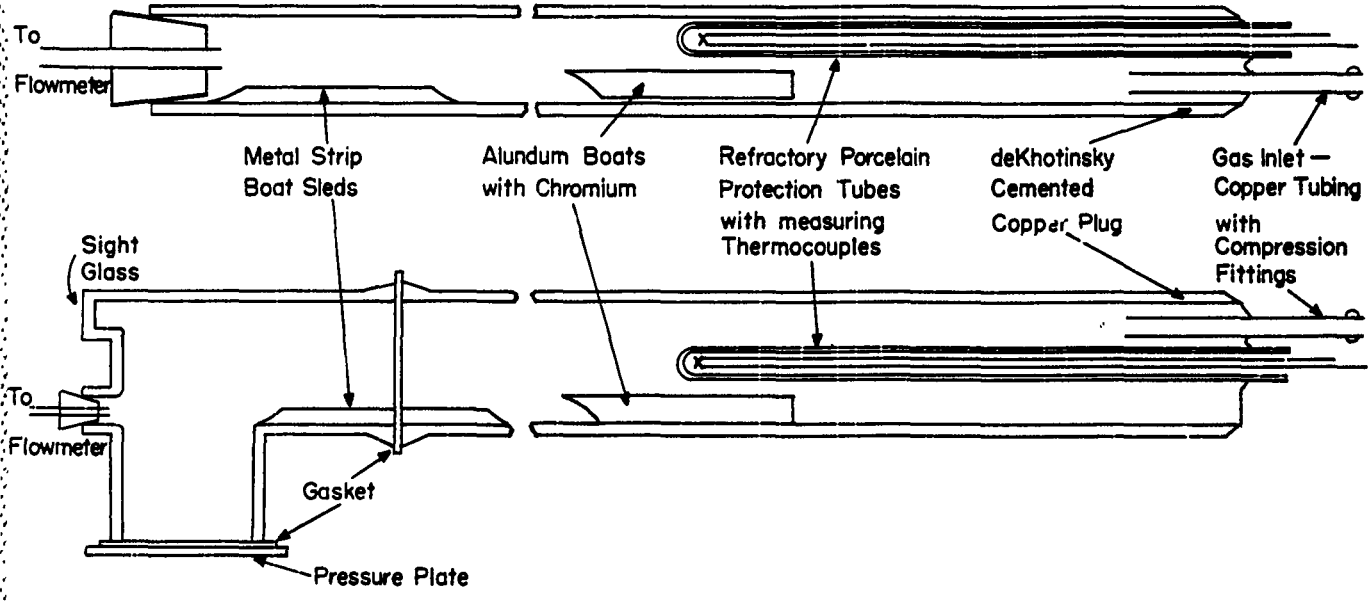


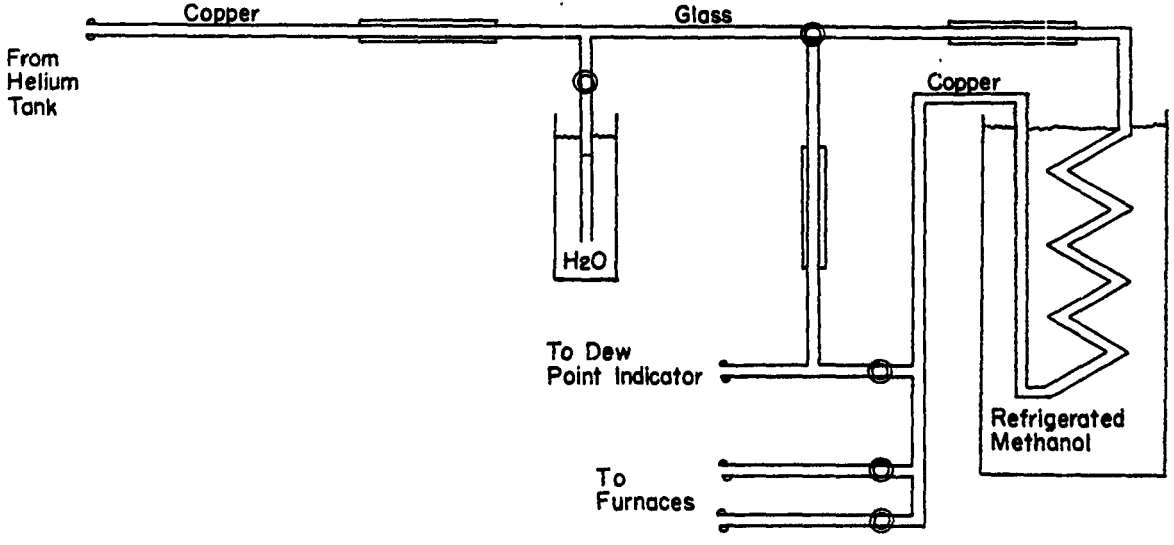
Schematic of Isotherm Method

Fig. 1



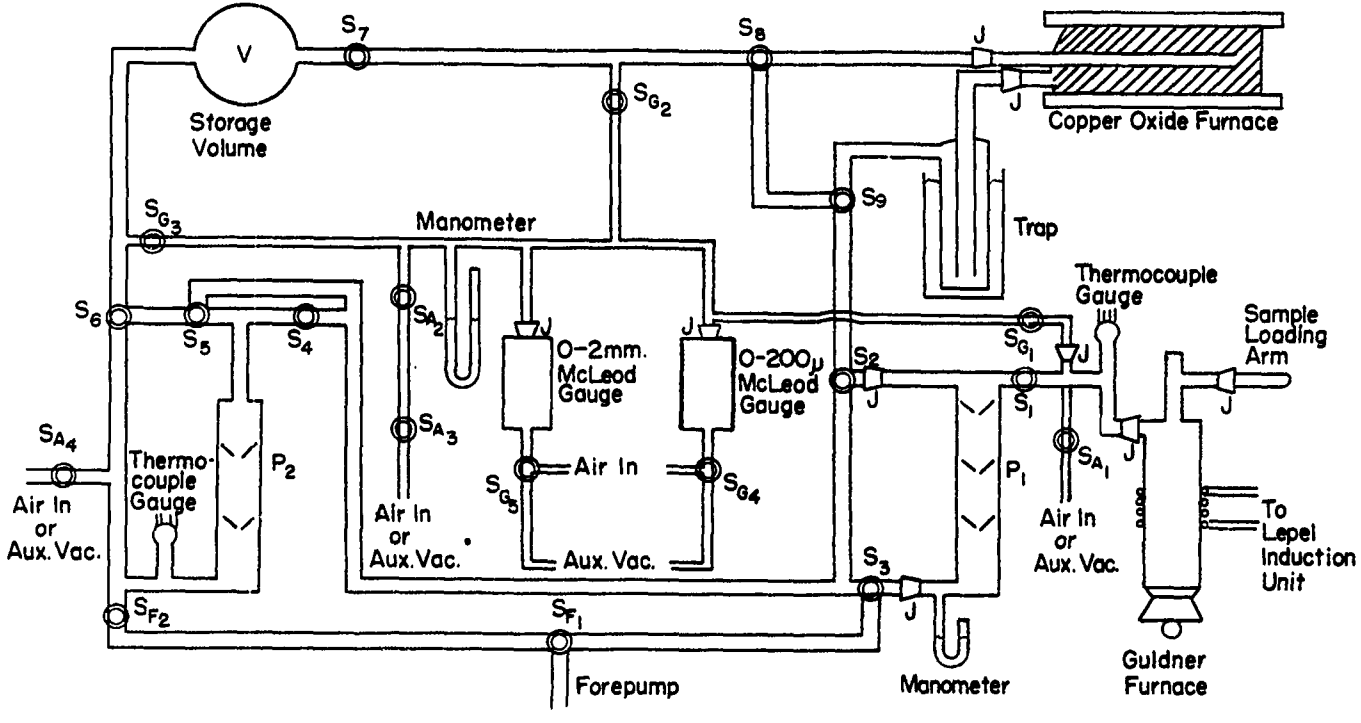
Sketches of Two Types of Combustion Tubes

Fig. 2



Sketches of Dew Point Controller and
Helium Distribution System

Fig. 3



Schematic of Vacuum Fusion Equipment

Fig. 4

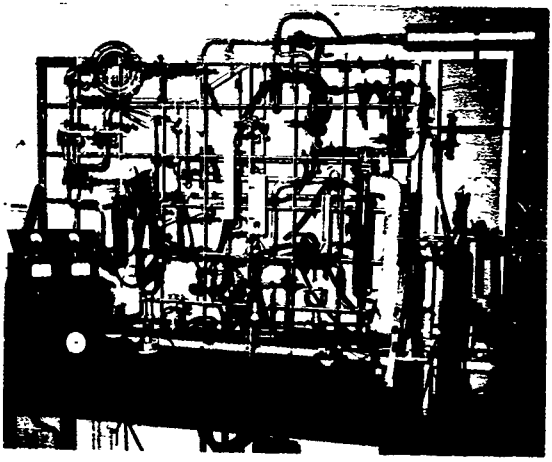


Figure 5. Vacuum Fusion Apparatus.

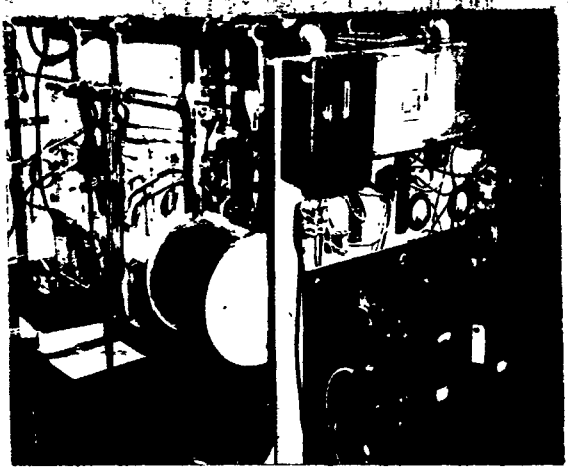


Fig. 6. Low Temperature Nitriding Equipment.

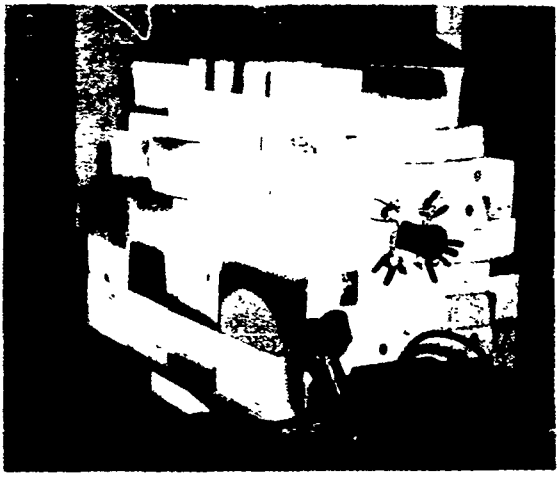


Fig. 7. High Temperature Nitriding Furnace.

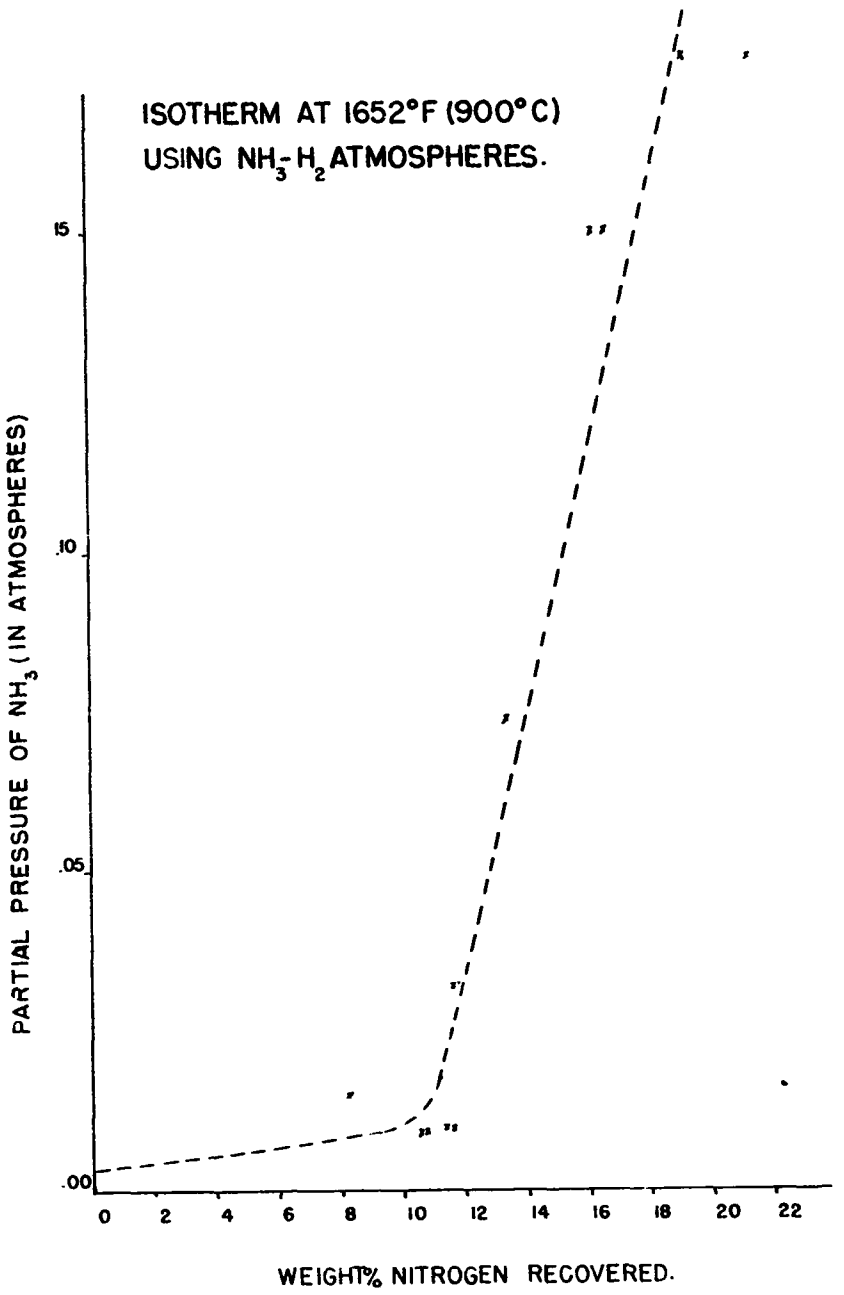

ISOTHERM AT 1652°F (900°C)
USING NH_3-H_2 ATMOSPHERES.
PARTIAL PRESSURE OF NH_3 (IN ATMOSPHERES)
.15
.10
.05
.00
0
2
4
6
8
10
12
14
16
18
20
22
WEIGHT% NITROGEN RECOVERED.

FIGURE 8

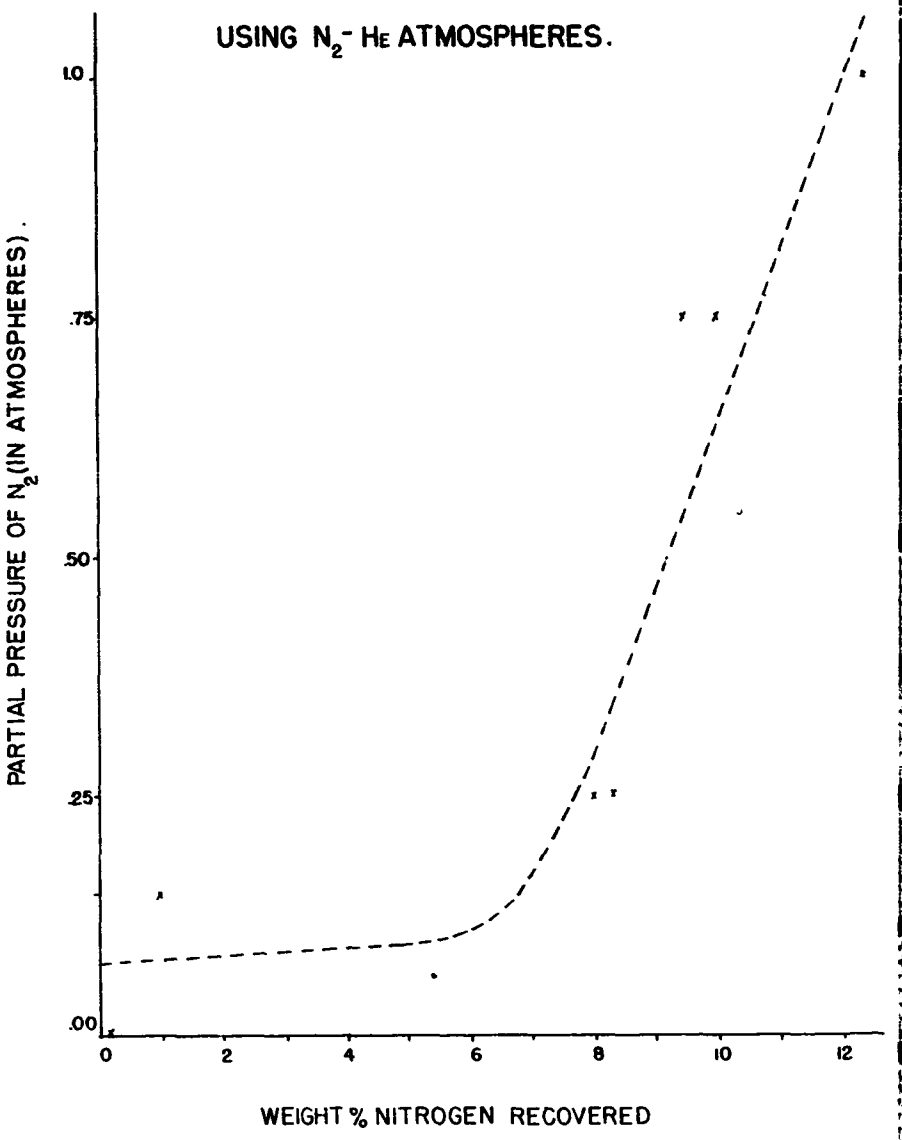

ISOTHERM AT 1460°-1485°C
USING N_2- He ATMOSPHERES.
PARTIAL PRESSURE OF N_2 (IN ATMOSPHERES).
1.0
.75
.50
.25
.00
0
2
4
6
8
10
12
WEIGHT % NITROGEN RECOVERED

FIGURE 9

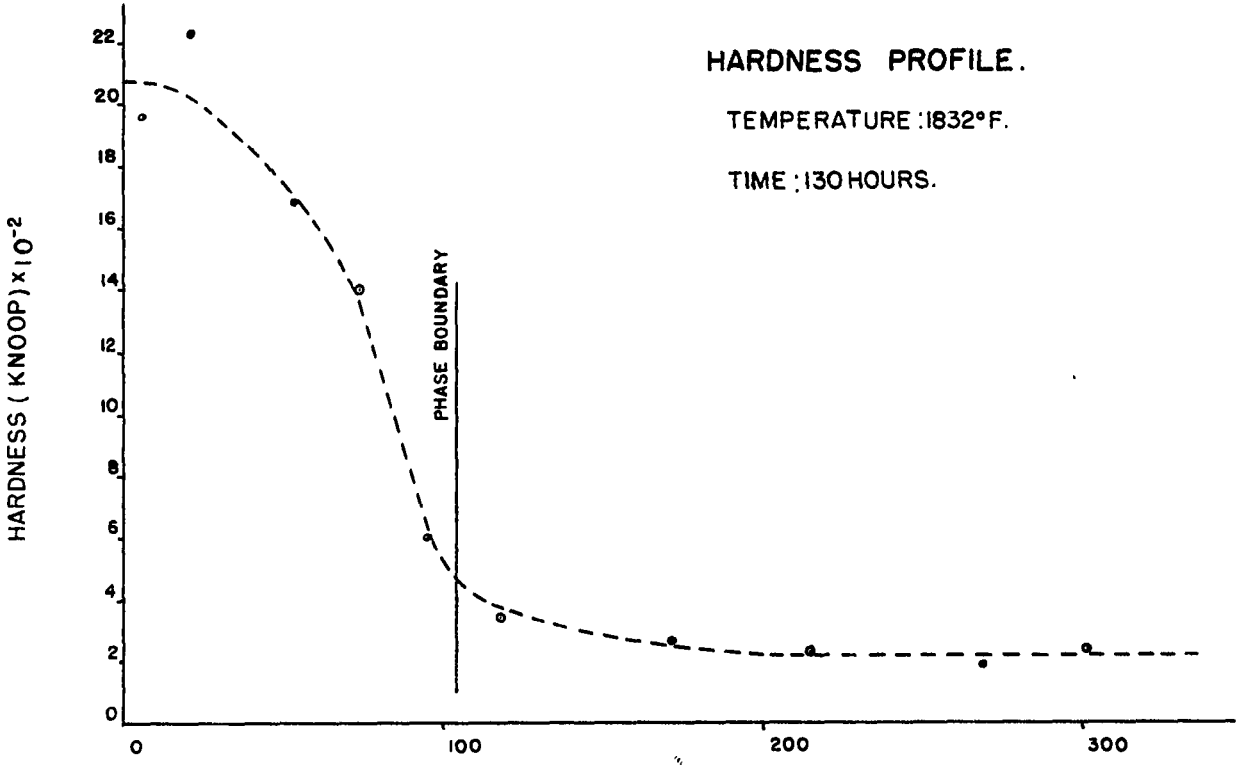

HARDNESS PROFILE.
TEMPERATURE : 1832°F.
TIME : 130 HOURS.
HARDNESS (KNOOP) x 10⁻²
PHASE BOUNDARY
0
2
4
6
8
10
12
14
16
18
20
22
0
100
200
300
MICRONS FROM SURFACE.

FIGURE 10.

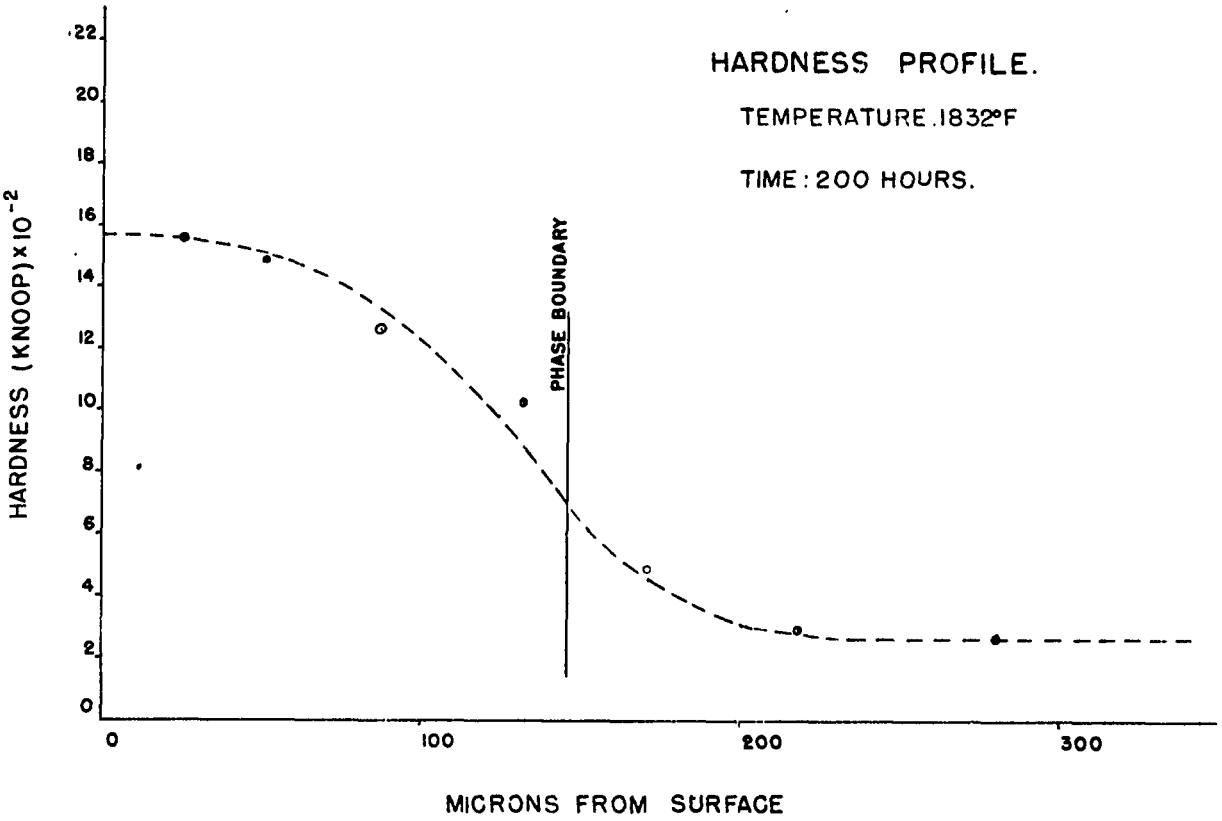

HARDNESS PROFILE.
TEMPERATURE 1832°F
TIME : 200 HOURS.
HARDNESS (KNOOP) x 10⁻²
22
20
18
16
14
12
10
8
6
4
2
0
PHASE BOUNDARY
0
100
200
300
MICRONS FROM SURFACE

FIGURE II

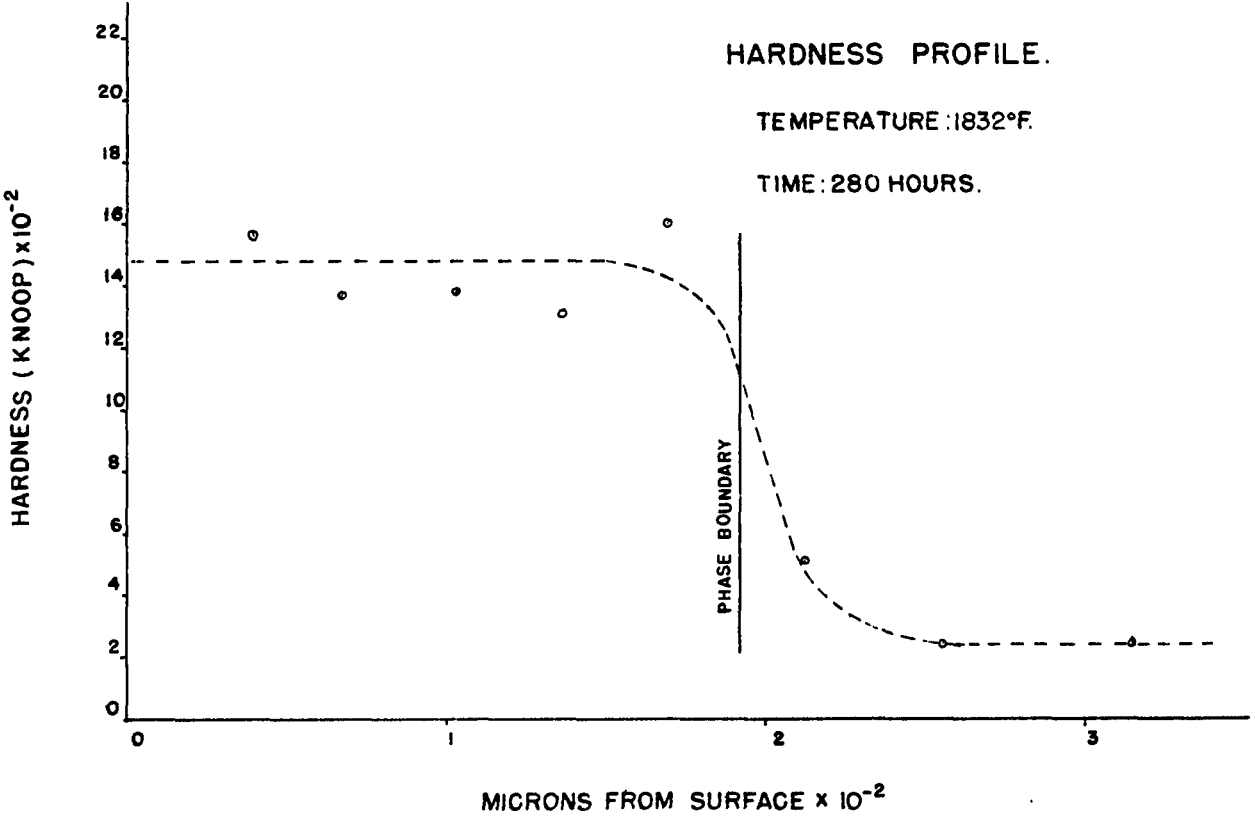

HARDNESS PROFILE.
TEMPERATURE: 1832°F.
TIME: 280 HOURS.
HARDNESS (KNOOP) x 10⁻²
22
20
18
16
14
12
10
8
6
4
2
0
PHASE BOUNDARY
0
1
2
3
MICRONS FROM SURFACE x 10⁻²

FIGURE 12.

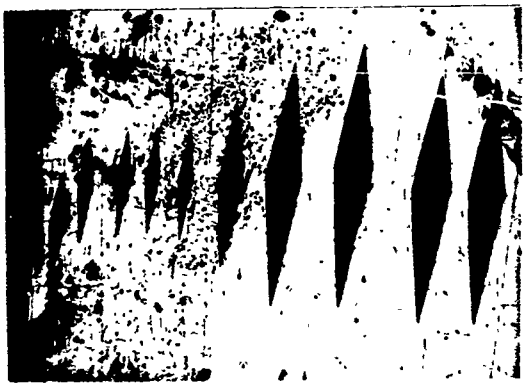


Fig. 13. Hardness Traverse of Nitrided Specimen.
The specimen is the one described, and plotted in Fig. 12.

THE WEIGHT INCREASE OF CHROMIUM WITH TIME IN A NITRIDING MEDIUM.

TEMPERATURE 1832° F

ATMOSPHERE: 100% NH_3

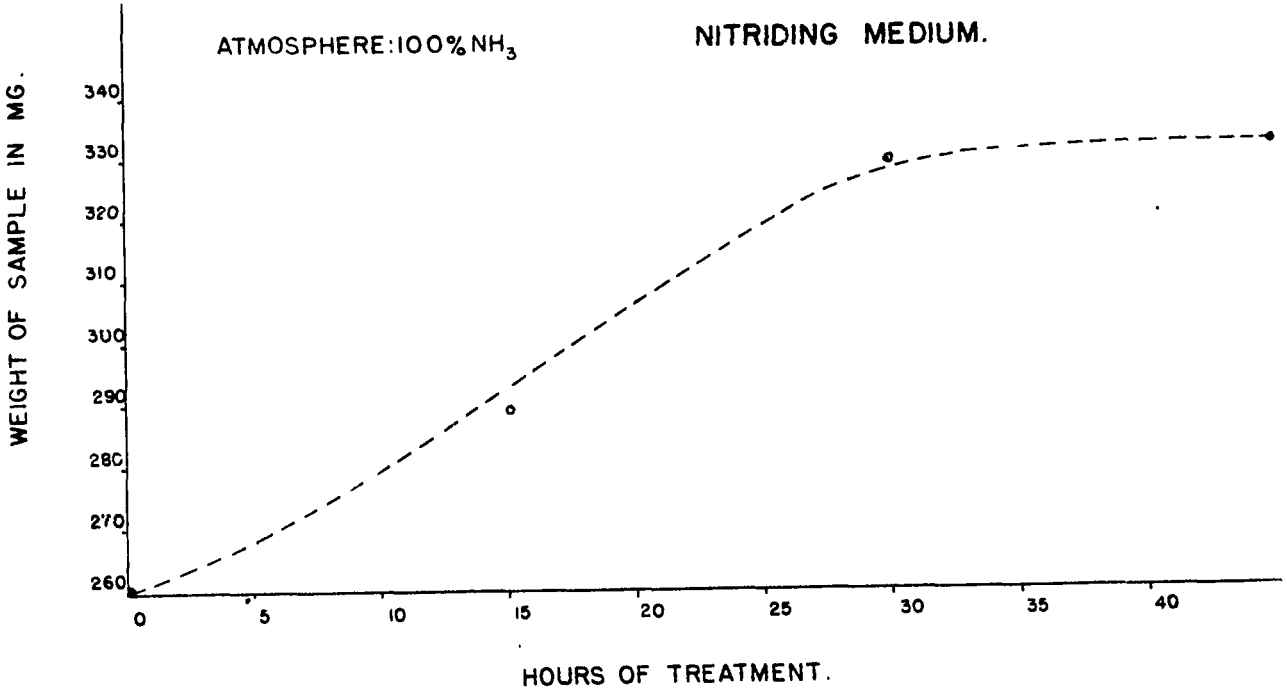


FIGURE 14.