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of

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The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Reuben Willett Cornell for the degree of Chemical Engineer They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Chemical Engineer.

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TITANIUM NITRIDE, PREPARATION, PROPERTIES AND USES

A Thesis

Submitted to the Graduate Faculty

of the

University of Minnesota

by

Reuben W. Cornell

In partial fulfillment of the requirements

for the

degree of

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Introduction:

Titanium Nitride as a substance of commercial importance has not found wide application as yet. It was at one time thought feasible to produce amonia from nitrogen of the air by first converting rutile into titanium nitride and then remove the amonia by boiling the nitride with caustic soda. The expense and difficulties encountered in the production of the nitride has served to put this method of fixing atmospheric nitrogen out of use. With the exception of this one attempt to utilize commercially titanium nitride no important use has come to the writer's attention.

It was observed, that, when titanium nitride was used as an electrode in sulfuric acid solution it produced valve action when an alternating current was sent through the cell - Ti_2N_2 - H_2SO_4 - Pb - the current was rectified to such an extent that it plated out copper on one electrode of the cell - C - $CuSO_4$ - C - placed in series with the former cell. This fact suggested a possible use for titanium nitride; namely as a rectifier for alternating current.

The nitride used in these observations was the silvery metallic compound of high density. It was very hard, scratching glass with ease, and had a nitrogen content of 36%. It was obtained from Mr. Whitney of the General Electric Company.

The problem in hand resolved itself into three parts. First, the most economical production of titanium nitride as described above. Second, the forming of the nitride into plates which could be used as electrode. Third, the determinating of the best condition for the operation of the cell-Ti_2N_2- H_2SO_4 - Pb - as a rectifier.

Part I

Preparation of Ti_2N_2.

The correct conditions for the production of metallic nitride of titanium proved to be more of a problem that was at first anticipated. Titanium nitride is an electric furnace product obtained by mixing correct amounts of rutile, titanium oxide and carbon; and subjecting the charge to the action of the electric arc in an atmosphere of nitrogen.

The reaction of the constituents is as follows

$$TiO_2 + 2C + N_2 = 2CO_2 + Ti_2N_2$$

According to Moissan (1) the correct conditions were 40 horse power or 70 volts and 350 amperes. Dr. Whitney stated in a letter from the General Electric Company that the nitride could be made by mixing a charge of Rutile, TiO_2 and carbon and subjecting it to a temperature of 1600°C in the electric furnace.

The nitride as produced, however, contained only a very small percentage of the silvery metallic product. The majority of the runs produced a purple or blue fused mass, probably a higher nitride and a brown clinker made up of very minute crystals of titanium carbonitride TiCTiN.

Twenty runs were made in an endeavor to make a satisfactory metallic nitride similar to the sample sent by the General Electric Company. Every condition of running was varied, including; furnace construction, time of run, voltage, amperage, type of furnace, constituents of charge.

The runs with their results will now be taken up in order.

Run I

Apparatus -	Electric furnace (crucible arc)
(Figure No. I)	N_2 tank and connections.

Method - The run was started from the cold material using 23 gms TiO_2
130 gms. Rutile
20 gms Carbon

Great difficulty was obtained in making an arc. Finally, however, after an addition of more carbon the run was made using a voltage of 25 - 35 volts, amperage of 200 - 400 amps. This run was of short duration, only $\frac{1}{2}$ hour being sufficient to complete the run. No nitrogen was run thru the apparatus as it was merely a trial of the furnace.

Results.

The final product contained a very small percentage of TiN intimately mixed with Rutile and carbon.

Conclusions:

(a) Charge must be preheated.

(b) N_2 is preferable but not absolutely necessary.

(c) Runs should be of longer duration.

(d) This furnace although not entirely satisfactory may be used for the production of TiN.

Run II

Run No. 2 was made as follows

Apparatus:

Electric furnace crucible - arc Figure I

N_2 Tank and connection.

Method:

A mixture of the following composition

500 gms Rutile
90 gms Carbon (powdered coke)

was preheated to semiredness in an iron crucible, after which it was dumped into the electric furnace crucible and a current of 300 - 350 amperes was sent thru the charge at a voltage of about 30 which was subsequently increased to 45 volts. At the end of two hours during the latter half of which N_2 was passed thru the melt, an endeavor was made to pour the mass. This attempt was a decided failure for the causes outlined below.

Results:

About two hundred twenty five gms. of product were produced. The product was impure, brittle, hard, of great density and high specific gravity.

A subsequent run, of about an hour on the mass of granular black residue which remained in the crucible after the Ti_2N_2 had been removed, showed that no more TiO_2 was left unchanged in the charge.

Conclusion:

(a) It was found that the arc of the furnace passed from the upper electrode to the side of the crucible thus preventing the passage of the arc thru the melt, and lowering the efficiency of the furnace.

(b) The Ti_2N_2 formed rose to the top of the melt and solidified very rapidly thus preventing a pouring of the charge and an incomplete transformation.

(c) By adding first an excess of carbon, air instead of nitrogen might serve for the nitrogen source.

(d) Finally an excess of Rutile should be added to act upon the carbon left, and then if the charge be heated for a sufficient length of time a pure product, capable of being poured, might be obtained.

Run III

Apparatus: Electric furnace #1 - crucible - arc
Source of compressed air and connection

Method:

A mixture of the following composition

Carbon	70 gms.	+ 70 gms. excess
Rutile	400 gms.	

was weighed out separately.

The carbon was added to the crucible and a current of 300 amps sent through the circuit at 25 volts. When the furnace became hot, the rutile was added in small portions with thorough stirring. The voltage was increased to 45 and air was run thru the melt. The run lasted about $1\frac{3}{4}$ hours with the following results.

Approximately 300 gms. of a very hard granular and brittle mass was obtained. Its color was light brown to black, similar to run no. 2.

Conclusions:

(a) A different type of electrode might serve better.

(b) Nitrogen gas produces much better results than air.

Run IV

Apparatus: Electric furnace #1 with the following changes; (a) graphite crucible was replaced by a fire clay crucible with a graphite electrode as the bottom; (b) a tube of graphite filled with copper filings was placed beside the crucible in a separate slot and the air was blown thru this tube into the charge, thus removing the oxygen and producing an increased percentage of nitrogen.

The conditions of the run were the same as in Run No. 3.

The results were the same as in Run III.

Conclusions:

Still further modifications need to be made before any successful results may be expected.

The fused nitride must be removed from between the electrodes as it short circuits the furnace.

A method current control must be found because the transformations of the charge produce substances of very different conductivities which makes a constant amperage impossible.

A more suitable means of producing nitrogen should be employed.

Run V

Apparatus: A core furnace was made up as shown in Figure 2. The core was 2 x 2 x 10". A current of air was forced over the top of the furnace.

Method: The core was made up of four parts of Rutile, one part TiO_2 and two parts carbon. The current was sent thru the charge **at** 60 volts and 300 amperes for four hours.

The product was in the form of nuggets of silvery colored metallic nitride covered with a layer of oxidized or carburized material, gray to brown in color.

Conclusion:

The following observations were made.

Conductivity of cold charge extremely low.

Conductivity of charge increases with increase of temperature.

Formation of Ti_2N_2 takes place with great acceleration when temperature of reaction is reached. Reaction is exothermic.

Conductivity of product when hot is high.

This method is the only one so far studied which will produce the silvery colored nitride.

Run VI

Apparatus: Same as in Run V

Method: Same as in Run V

Product: The yield obtained was poor, consisting of small fused particles of the silvery nitride covered with the black carbide and larger particles of the bronze carbonitride also covered with the carbide.

Conclusions: A pure mixture of the Rutile and TiO_2 and carbon must be used to produce a good uield of the nitride. At least 1½ hours should be allowed to heat up the charge. The charge should be kept uncovered and not compressed.

Run VII

Apparatus: Indirect arc furnace as shown in Figure 3 electrode $\frac{3}{4}$" diameter crucible 3" diameter.

Method: A mixture of four parts Rutile, one part TiO_2 and one part carbon was heated by means of the indirect arc for 30 minutes at a voltage of 40 - 60 and an amperage of 300.

The product was a semi-fused mass of yellow and silver particles coated with carbide. Much of the charge remained unchanged.

Conclusions:

The electrode points must be carefully sharpened for best results.

A shallow crucible of graphite is the best type to use.

As high a voltage (giving a maximum temperature) should be used.

Runs VIII & IX

Apparatus: Same as for Run VII

Method: A charge of Rutile 4 parts, TiO_2 1 part and carbon 3 parts was used. In the bottom of the crucible was placed a layer of NH_4NO_3. It was thought that following reaction would take place.

$$NH_4NO_3 = 2H_2O + N_2O$$
$$N_2O + C = 4N + CO_2$$
$$4N + 4TiO_2 = 2Ti_2N_2 + 4O_2$$

The furnace was run for thirty minutes at 200 - 300 amperes and 40 volts.

The product in both cases was a semi fused mass of bronze and red colored particles.

Run No. 8 was made with an insufficient amount of carbon in the charge but this did not alter the result.

Conclusions:

In order to obtain better fusion an increase in temperature (voltage) will be necessary.

At the temperature used, however, NH_4NO_3 volatilized too rapidly for satisfactory results.

Run X

Apparatus: A combustion tube and furnace with compressed air connections.

Method: An attempt was made to produce Ti_2N_2 in a combustion furnace. The charge of four parts of Rutile, one part TiO_2 and one part carbon was placed in one end of the combustion tube and heat was applied. Copper turnings were placed in the other end of the tube and also heated. Air was blown over the copper (the oxygen being thereby removed) and thence passed over the heated charge to effect reaction. The charge was unchanged after 2 hours heating.

Conclusion: The nitride cannot be formed in a combustion tube, open furnace from TiO_2, Rutile, carbon and N_2 since a high enough temperature cannot be produced.

Runs XI & XII

Apparatus: Indirect arc Furnace as shown in Figure 3. A shallow graphite crucible with a slotted depression in the bottom to collect any part of the charge which might fuse and flow.

Method: These runs were an attempt to attain an extreme temperature in order to cause the nitride to flow or fuse at least when it formed. A mixture of 150 gms. TiO_2, 100 gms. Rutile, 50 gms. carbon was placed in the crucible. Air was forced in from the top. The runs were made for 30 minutes at 30 - 40 volts and 300 - 400 amperes which was the capacity of this furnace.

Run No. XI showed only a mixture of unfused charge and a small amount of purple and yellow fiable powder.

In Run No. XII the results were much better but not entirely satisfactory. A heavy coating of fused Ti_2N_2, which exhibited valve action, was obtained. This mass was very brittle, iron colored and crystaline. It was covered with an oxide coating.

Conclusions: These runs show that Ti_2N_2 can be produced in this way, but not cast, as the product solidifies on formation and does not flow.

Run XIII

Apparatus: Core furnace as shown in Figure 2. Size of core 4" x 3" x 3".

Method: The core was made up of one part carbon, one part TiO_2 and one part Rutile. Air was forced in from the bottom by mean of a graphite tube. The run was made at 60 - 40 volts - 200 - 600 amperes for one hour and twenty minutes.

The product consisted of the usual colored mass - green, bronze and black, together with a small amount of very porous globules of silvery luster.

Conclusion: The silvery metallic nitride is best produced in this type of furnace.

Runs XIV & XV

Apparatus: Same as Run No. XIII

Method: The core was made up with a mixture of one part carbon, one part TiO_2 and two parts Rutile. Air was forced in from the bottom. The run was made at 60 - 40 volts - 200 - 400 amperes for one and one-half hours.

Both of these runs produced the metallic nitride with the silver color. The first run contained only a few globules intermixed with much black residue. The second run, however, was more successful showing a good amount of dense metallic substance around the carbon cores.

Conclusions: This run proved that the core furnace method produces titanium nitride successfully.

Runs XVI & XVII

Apparatus: A resistor furnace was used as in the above run No. XV. Graphite was used as the resistor and a graphite tube was inserted horizontally in the graphite and at right angles to the charge. The charge of two parts of rutile, two parts TiO_2 and one part carbon was placed in the tube. Preheated air was led into one end of the tube and was drown out the other end. The run was made at 40 - 60 volts and 300 amperes for one hour and twenty minutes.

The run was made to determine if the volume of air passing through the charge and its contact surface with the carge affected the results materially.

The product from the first run, when a tube of 3/8" diameter was used, produced the usual purple powder with a yellow powder and a small amount of fused particles. The second run used a 5/8" tube. It was of little value since the charge was only partially transformed and no nitride was observable.

Conclusion: The poor results here obtained show that the volume of air and its contact with the charge are of little importance. This may be corroborated by the good results obtained in a resistor furnace where a limited amount of air reaches the charge.

Run XVIII

Apparatus: An Arsem vacuum Arc furnace.

Method: The prupose of this run was to determine whether high temperatures (2,000°C) and above were necessary to the formation of the nitride. Although the furnace was a vacuum arc type, enough air was allowed into the furnace to supply the necessary nitrogen. The charge, one part TiO_2, one part Rutile, one part carbon, in a crucible 2" high by $\frac{3}{4}$" diameter was run at 7 - 10 KW for 50 minutes.

Conclusion:

This run showed conclusively that the formation of the nitride was not dependent on excessive temperatures, because, the product was of the usual purple and brown clinker type without any silvery metallic appearance.

Runs XIX & XX

Two runs were made using the furnace made up in Run XVII. Instead of forcing air through the crucible tube, preheated amonia gas was forced into the tube. A slight suction was attached to the other end of the tube. It was thought that by preheating NH_3 it would break down in the electric furnace to form nitrogen and hydrogen. The former would react with the titanium which would be liberated by the combination of the oxygen of TiO_2 with the hydrogen formed. The amonia was generated in a flask by adding NH_4Cl to NaOH. The runs were made at 40 -60 volts and 300 amperes.

The product was a black porous clinker with much unchanged oxide. No fusion seemed to have taken place.

Conclusion:

The use of NH_3 to reduce the oxide in preparation for the formation of the nitride by means of the nitrogen of decomposition does not seem to be possible judging from the results of these tests.

The results of these runs show little of real practical value. Titanium nitride, the silver metallic substance of hardness equal to the diamond and density of 5.1 can be produced in the electric furnace under exact conditions. The maximum yield has not been attained because the correct conditions have not been absolutely determined. However, for the highest yield a resistor furnace with a small core about 2" x 2" x 6" should be used. Equal quantities of Rutile and TiO_2 and ½ unit of carbon preferably coke, should be used.

The amperage should be about 300 - 400 and voltage about 60 or 70 if possible. The nitride will form at the hottest point of the furnace so that the heat must be concentrated as much as possible. Nitrogen gas as the source of nitrogen is the best agent to use but air will suffice. The reaction is exothermic and may be noted by the flows produced. When the reaction has ceased the furnace may be shut down and the charge cooled and drawn. This ought, with careful regulation, to produce a fair amount of metallic titanium nitride.

Part II

Casting the Nitride into Plates Suitable for Anodes.

The literature on this subject is entirely lacking. No melting point is known for Ti_2N_2 and as a consequence some doubt was felt that the compound could be melted and cast. It is of interest to know that the nitride decomposes (Friedel & Guerrin -2-) when the amperage of the electric furnace is increased from 300 to 1000. The nitride changes to the carbide. Also of minor importance is the fact that aluminum nitride, whose properties are very similar to the compound being studied, has no melting point but decomposes at 2200°C.

Nine runs were made in electric furnaces at the highest temperatures attainable and under as varied conditions as were possible to obtain the nitride in the molten condition. Following are the results of the various runs.

Runs I, II & III

Apparatus: Indirect arc as in Figure 2.

Method: A mixture of impure Ti_2N_2 and Rutile, TiO_2 and carbon was placed in a shallow graphite crucible. The fresh charge was added since the reaction to form the nitride is an exothermic one and this would aid in increasing the temperature. The run was made at 300 amperes, 30 - 50 volts for sixty minutes. The products as placed in the furnace were unchanged except for oxidation or carburization on the surface.

Conclusion: Due to improper design of furnace, poor design of crucible and poor electrode points, these runs gave results which were of no value.

Runs IV, V & VI

Apparatus: Resistor crucible furnace as shown in Figure III

Method: Impure Ti_2N_2, Rutile, TiO_2 and carbon in equal parts were mixed carefully and placed in a crucible which in turn was placed in the resistor carbon. The furnace was run two and one-half hours at 40 - 60 volts and 300 amperes.

The product was unchanged. There was a small amount of surface decomposition on the Ti_2N_2. The particles were covered with a white coating of TiO_2.

Conclusion: Due to the large size of the furnace used, the necessary heat to melt the Ti_2N_2 could not be obtained in the resistor furnace. The crucibles used were of three kinds, graphite, fire clay, and carbon, silica mixture. Of these the graphite stood up under the heat the best, but was corroded by the charge to some extent by the formation of the carbonitride.

Runs VII & VIII

Apparatus: Resistor furnace as used in previous runs and graphite crucible.

Method: The fused mass from runs III & IV in the production of $Ti_2N_2$was heated up in a graphite crucible at 300 amperes and 40 volts for two hours. The mass clinkered but refused to melt so far as to flow. This clinkered mass was reheated in the same manner with some pure TiO_2. The same time and energy were consumed. The results were lost as the crucible bottom was destroyed and the charged mixed with the graphite in the furnace. No melted pieces of nitride were found in the furnace carbon, however.

Run IX

Apparatus: Resistor furnace as used in runs V-VIII. A crucible was used whose dimensions were $\frac{3}{8}$" x 3" with a tight fitting cover.

Method: A mixture of impure titanium nitride, produced in previous runs, and an equal portion of the pure nitride from the General Electric Company was placed in the small graphite crucible and the cover was forced tightly into the top. This size and type of crucible was chosen to concentrate the heat on a very small charge, and also to prevent primary oxidation of the charge. The crucible was buried in the resistor carbon to a depth of about three inches. The furnace was then heated for forty-five minutes at 40 - 60 volts and 300 amperes.

The product showed no change in the original charge, except oxidation on the surface and a slight transformation to the bronze colored carbonitride $TiC\ Ti_2N_2$.
Conclusion: This run was made with the idea of obtaining the highest temperature possible in an electric furnace. The nitride was not melted under these extreme conditions which brings forth the conclusion that it cannot be melted commercially.

Finally an attempt was made to fuse the nitride by using the compound itself as electrodes of an arc. During the passage of current (A.C.) a gas, probably nitrogen, was given off. The two electrode became fused but on close examination it was observed that the fused portion had been broken down to the white oxide. The only conclusion which chould be drawn from these tests is that titanium nitride is not capable of being melted and consequently cannot be cast into plates, once it has been formed. The only alternative is to cast the substance just as it is being formed and in this way shape it as desired.

Part III

Conditions of Rectification and Properties.

So much time was spent on determining how to made the nitride that little time remained in which to study the properties and conditions for rectification. Several rough determinations were made on the properties of the nitride supplied by the General Electric Company. They are as follows:

I-Rectification

To determine the rectification which a titanium nitride electrode in sulfuric acid produces, the following set-up was used, (see figure 4). Alternating current was tapped from 110 volt mains and led thru a transformer with an A. C. ammeter, a D. C. ammeter and the cell - Ti_2N_2 - H_2SO_4 - Pb - The A. C. ammeter read the effective amperage and the D.C. ammeter the rectified current at its average value. That is, if complete rectification took place the A.C. reading would equal the D.C. reading times 1.11 which is the form factor.

The following tables show the results.

Test #1

Amps A.C.	Amps D.C.		Rectification
0.130	.005		4.26%
0.250	.005		2.22%
0.500	.008		1.77%
0.750	.0125		1.85%
1.000	.020		2.22%
1.50	-.03	Reverse Polarity	2.22%
2.000	-.02		1.11%
2.50	+.04	Reverse Polarity	1.78%
3.00	+.08		2.96%

Test #2

Amps A.C.	Amps D.C.		Rectification
.5	0.005		.11%
1.0	0.020		2.22%
1.5	0.040		2.96%
2.0	0.040		2.22%
2.5	0.000		0.0%
3.0	0.020	Reverse Polarity	.74%

Test #3

Amps A.C.	Amps.D.C.		Rectification
.5	0.0025		0.55%
1.0	0.0065		0.72%
1.3	0.060		5.13%
1.5	0.030		3.70%
1.7	0.025		1.63%
2.0	0.015	Reverse Polarity	.83%
2.2	0.040		2.02%
2.5	0.070		3.11%
2.8	0.040		1.58%
3.0	0.016		0.59%
3.1	0.005		0.18%

The results obtained are very interesting. They show that commercially rectification by this cell is impossible. The unusual mode of rectification first in one direction and then in the other as amperage increases is a phenomenon worthy of more study than can be given it at this time. The change of direction of rectification is probably due to a mixture of nitride or impurities exerting their influence under the changed conditions. A series of graphs was made from the data in order to bring out this peculiar action more clearly.

In order to check up these results, the same type of cell was tested by means of the oscillograph. Tracings were made of the curves which were obtained. The interpretations of these curves show that rectification due to this cell is small; not over 5%, since there is no flattening of the current or voltage curves. It also shows that the cell has some capacity since the current curve leads the voltage by a small amount.

These two tests prove conclusively that Titanium Nitride in sulfuric acid does not have valve action to exceed 5%.

II - Corrosion Tests

The second property to be studied was the effect of acids and alkalies on the metallic nitride obtained from the General Electric Company. A sample was ground to pass a 20 mesh screen but remain on a 60 mesh screen. This uniform product was weighed out in 1 gm. smaples and each sample was placed in 50cc of a certain acid or base. The period of solution was seven days, temperature constant and evaporation reduced to a minimum. At the end of this time the solvents were filtered off and the unaffected nitride was washed into a gooch, washed with H_2SO_4 (2N) to remove any TiO_2 formed, dried and weighed. The tabulated results show that aqua regia is the only solvent which dissolves the nitride to any extent. The seemingly increased weights from the action of KOH & NH_4OH on the nitride are due to the action of the H_2SO_4 washing solution on the base which was left on the nitride by adhesion. The products formed could not be washed off completely and an increase in the weight of the sample was recorded. Further tests varying the concentration and temperature of the solvent would prove interesting but time was not allowed for those experiments in this work.

Corrosion Test

Sample No.	Wt.	Solvent	Strength	Wt. of Residue	% Dissolved
1	1.0016 gm	NaOH	1.5 N	1.0013	0.01%
2	1.0010	NaOH	1.5 N	0.9983	0.27%
				Av.	0.14%
3	1.0000	HNO_3	12 N	0.8932	1.068%
4	1.0000	HNO_3	12 N	0.9030	0.970%
				Av.	1.019%
5	1.0007	HCl	11 N	0.9833	1.73%
6	1.0008	HCl	11 N	0.9809	1.98%
				Av.	1.86%
7	1.0004	Aqua Regia	11.2 N	0.4840	51.61%
8	1.0009	Aqua Regia	11.2 N	0.5227	47.78%
				Av.	49.69%
9	1.0019	H_2SO_4	2 N	0.9909	1.09%
10	1.0000	H_2SO_4	2 N	0.9847	1.53%
				Av.	1.31%
11	1.0000	NH_4OH	9.5 N	1.0034	-0.34%
12	1.0002	NH_4OH	9.5 N	1.0033	-0.31%
				Av.	-0.32%
13	1.0000	KOH	2 N	1.0046	-0.46%
14	1.0020	KOH	2 N	1.0120	-0.99%
				Av.	-0.78%

III - Resistivity

The third property of the titanium nitride from the General Electric Company to be studied was its resistivity. Two tests were carried out for this purpose. The Wheatstone method of determining the resistivity was used in both tests. In the first experiment a tube of nitride ground to pass a 60 mesh screen was tested as to its resistance. This was done because of the difficulty of obtaining a uniform sized piece of the nitride as a solid. The tube was 5 cm. in length and $9\frac{1}{2}$ mm. internal diameter, sealed at both ends with a cork through which passed a copper wire. This tube was found to have a resistance of 40.4 ohms which gave the powder a resistivity of 5.72 ohms. According to the equation $R = \frac{r \times a}{l}$, where r is the resistance, a the area and l the length of the piece studied. In the

the second experiment a piece of solid nitride was used whose resistance was found to be 0.035 ohms. The piece was 14 x 5.5 x 4 millimeters in size and was held to the copper leads by a clamp. The resistivity of this nitride would be therefore 0.055 ohms. Its conductivity 18.2 mhos. Their value is only approximate as the method used is a rough one and the determinations are only to be considered as relative values.

The data for these tests follows:

60 mesh powder

	I		II		III	Av
Resistance	40.2	-	40.5	-	40.5	40.4

Resistivity

$$\frac{40.4 \times \frac{.95^2}{4} \pi}{.5} = 5.72 \text{ ohms.}$$

Solid piece

	I	II	III	Av
Resistance =	0.031	0.043	0.037	.035

$$\text{Resistivity} = \frac{-035 \times 5\frac{1}{2} \times 4 \times 10}{14 \times 10} = .055 \text{ ohms}$$

$$\text{Conductivity} = \frac{1}{.055} = 18.2 \text{ mhos.}$$

The conclusion which may be crawn from these tests is that the conductivity for titanium nitride is very high for this type of compound. (Al N = $.5 \times 10^6$) (Ti = 31.3) (Cu = 331.1) ($AgNO_3$ = 1.11) (3).

IV

An endeavor was made to determine the nitrogen content of the titanium nitride obtained from the General Electric Company and also that produced in this work. The only literature on the subject was found in Berechte Vol. 42 p. 900, and 909 which states that the nitrogen content of pure Ti_2N_2 can be determined by powdering the product and mixing 2 - 3 gm. CuO with it in a porcelain tube.

Then carefully heat the tube to 1000°C in an atmosphere of CO. Four attempts were made to do this by using a CO_2 tank as the source of gas and leading the gas into one end of a combustion tube containing the charge. The products together with some CO_2 was drawn off at the other end of the tube and collected in a bottle. The first two results were of no value because the samples were not analyzed at once and air was admitted which produced erroneous results. The data for the last two is given below.

Sample	Wt. Sample	Gas Collected	% N_2 in Gas Correct to 0° 760 m m	% O_2 Correct
G. E. Ti_2N_2	1.0377	750 cc	43.5%	7.48%
T_2N_2 produced in Resistor Furnace	0.7241 gm.	1400 cc	29.0%	7.01%

Sample	gms N_2	% N_2 in Sample	%N_2 in Sample -N_2 from air (note)	Formula
G. E. Ti_2N_2	0.37	35.3	13.7%	Ti_2N_2 2.2% N_2
Ti_2 N_2 produced in Resistor Furnace	.457	63%	5.8%	------

(Note) Assuming that O_2 in gas came from an external source the nitrogen which accompanied the O_2 $(= \frac{79.1}{20.9} \times O_2\text{vol.})$ was subtracted from the total nitrogen found.

These results show a wide variance due not only to inaccurate manipulation but also to non-uniformity of sample. The results, however, led to the conclusion that the nitride might not be a definite compound but only a solution of the nitrogen in the metal. To prove this point, a fifth test was made; namely, a study of the Micro-structure of Titanium Nitride.

V - The Micro Structure of Ti_2N_2

A sample of the compound from the General Electric Company was polished in the usual manner except that the initial polishing and grinding has to be done under water. This method has to be resorted to because the sample was very brittle and dry polishing would cause minute particles to flake off which in turn would cause elevations in the surface to be examined. This would make it impossible to focus the sample satisfactorily.

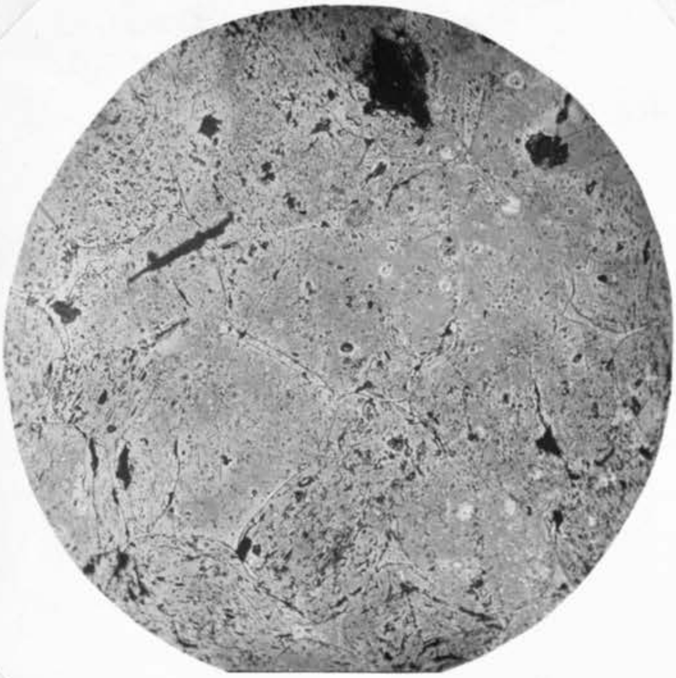
A view of the polished sample showed a smooth field without structure of any kind. Etching was resorted to. The following reagents were given three minute tests without success; KOH, NaOH, HCl, HNO_3, Aqua Regia. The sample was then given an extended treatment with Aqua Regia (35 minutes) and the view obtained, a photograph of which is included in this paper. The crystal boundaries are brought out clearly. That is all that may be definitely determined from this brief test except that it is unlikely that the nitrogen is in solution in the titanium since no eutectic mixture is apparent. The metal seems perfectly homogeneous, even after etching, which favors the idea that Ti_2N_2 is a definite compound, although more evidence is necessary for proof of the above statement.

Conclusion:

Before drawing any conclusion it might be well to state that several observations were made of the cell (Ti_2N_2 - H_2SO_4 - Pb) under the action of the electric current. When alternating current is passed through such a cell little rectification takes place at first, as noted by copper depositing out on one electrode of the cell (C - $CuSO_4$ - C). If, however, the voltage is increased to such a point that gas is given off at the titanium nitride electrode a thin brown oxide film forms on the surface. This changes the cell to the one (Ti Oxide - H_2SO_4 - Pb) and this cell has greater rectifying properties.

If time allowed, an actual proof might be made of the statement which would, undoubtedly clear up the phenomena noticed under the rectification tests, namely; reverse rectification with increasing amperage. This observation will furnish a problem for further research.

MICRO-PHOTOGRAPH



TITANIUM NITRIDE

Sample:
Ti_2N_2 obtained from the General Electric Co.

Properties:
Hardness equal to that of the diamond.
Silvery, metallic luster.
Very brittle.
Large crystals

Preparation:
Ground with 000 emery cloth (under water). Polished with rouge.

Etch:
Thirty five minutes in aqua regia

Results:
Crystal Boundaries brought out clear
Uniform composition of sample noted
Probably a pure chemical compound

As to the results of this paper, they have been tabulated at different points but to sum them all up, it might be said that Titanium Nitride may be produced in the electric furnace though with some difficulty. It cannot be cast but must be shaped as it is formed. Its rectifying properties within itself are of little value from a practical standpoint but from a theoretical viewpoint, together with the formation of an oxide layer, furnish a very interesting problem.

The corrosion test are of no little importance since they show the extreme resistance of the metal to the action of acids and bases.

The conductivity measurements, though crude, indicate that a high conductivity can be expected from this compound, which is unusual for this type of substance.

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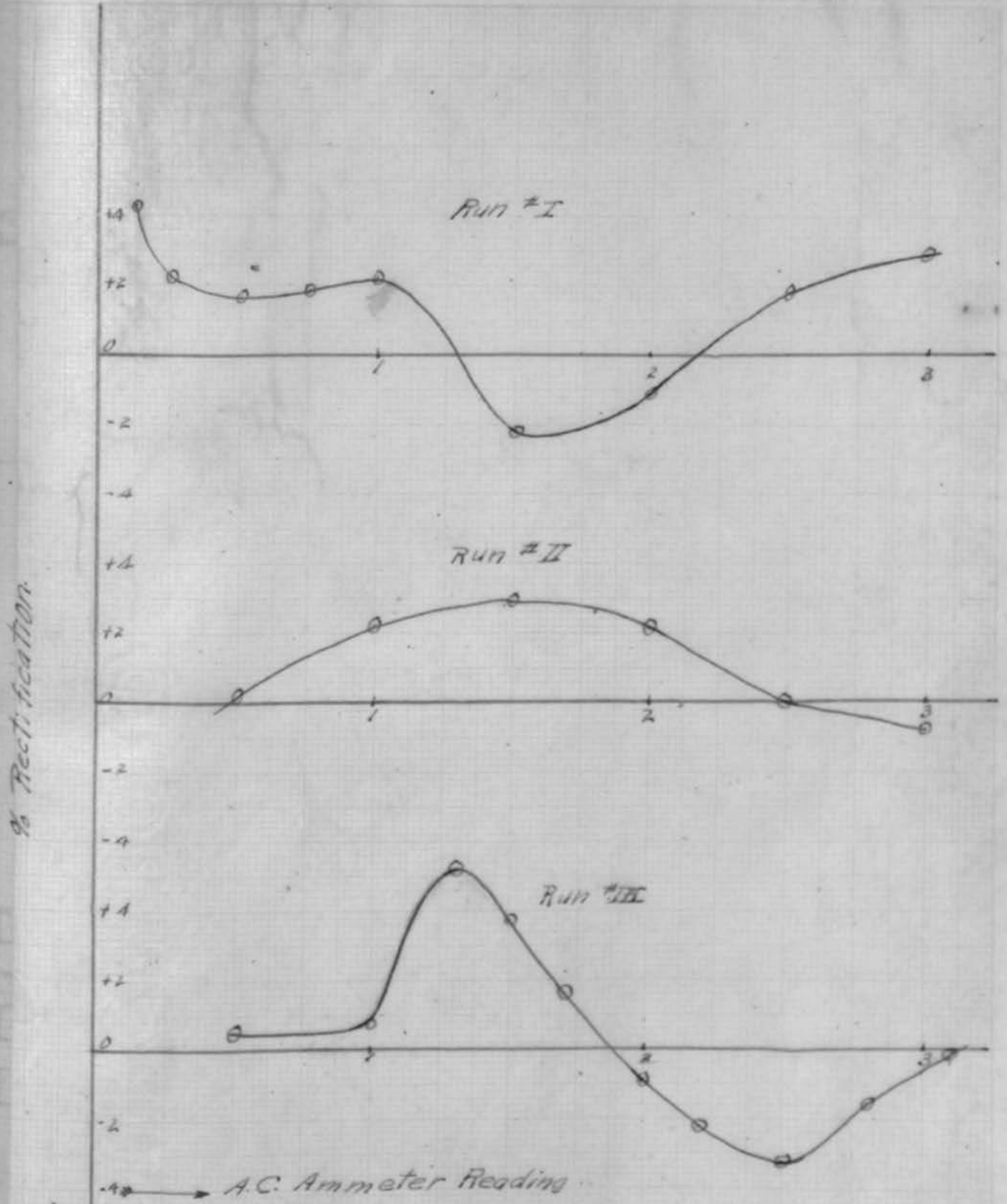


Curves Showing
Rectification in Percent
With change of A.C. current
By Means of Cell $[Ti_2N_2 - H_2SO_4 - Pb]$

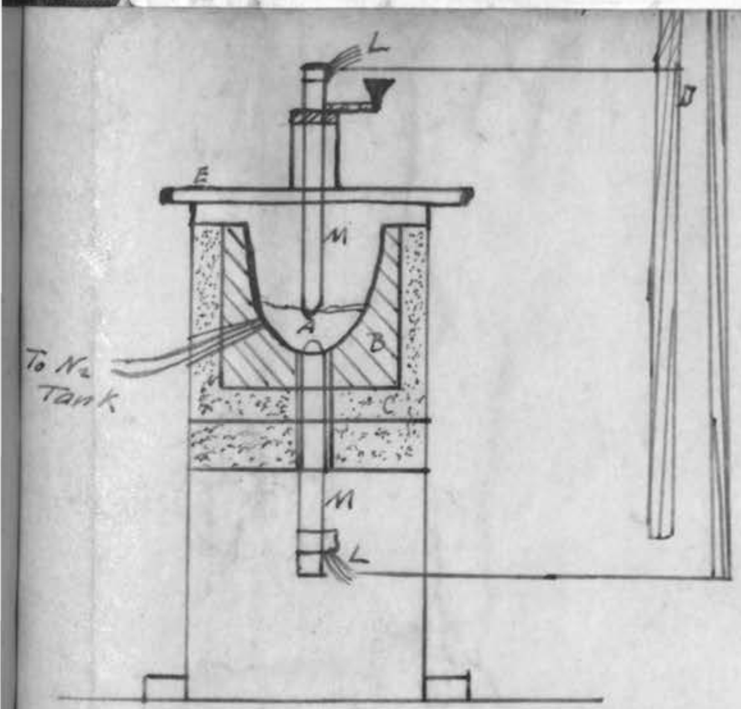


Fig I - Direct Arc Furnace

A = Charge
B = Graphite Crucible
C = MgO Packing
M = Graphite Electrodes
D = Bus Bars
E = Cover (Asbestos
L = Leads

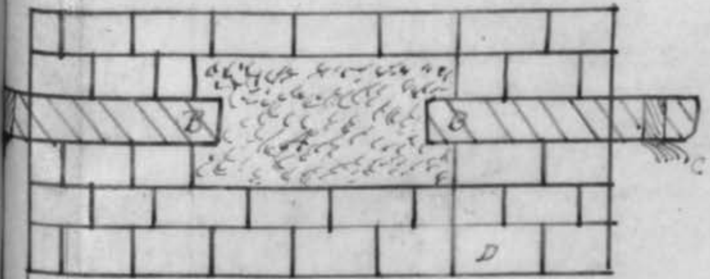
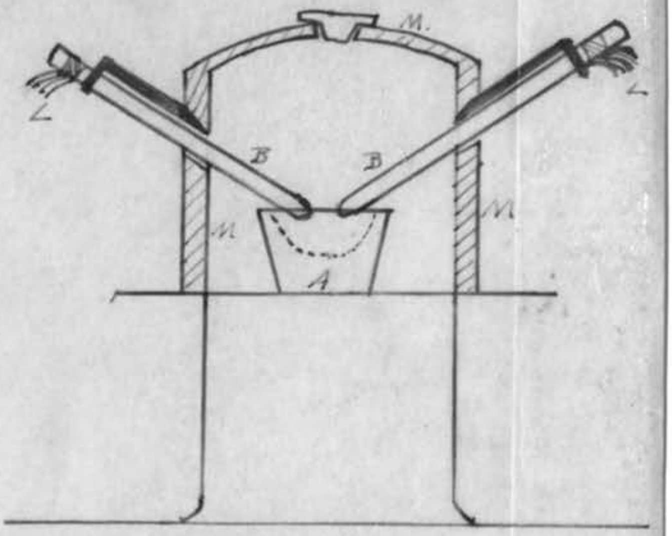


Fig II
Resistor Furnace

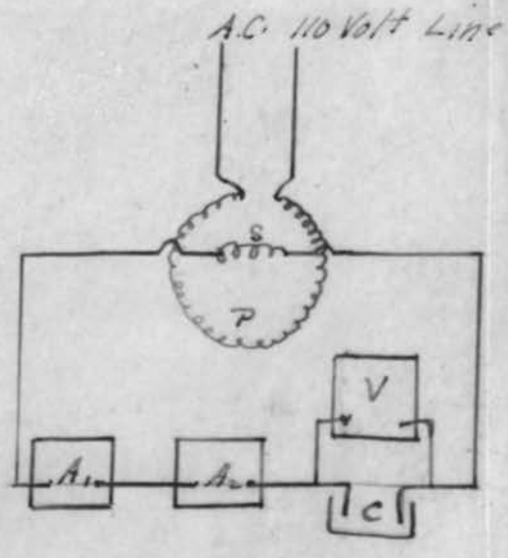
A = 1. Core
2. Resistor Carbon containing a crycible
3 Resistor Carbon containing a horizontal graphite Tube
B = Electrodes
C = Leads to bus bar
D = Silica brick wall

Fig III
Indirect Arc Furnace

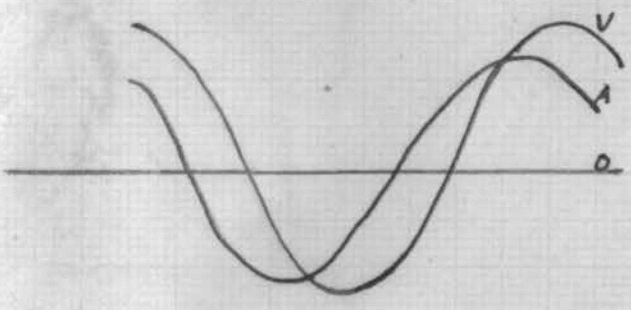


A = Crucible
B = Electrodes
L = Leads to bus bars
M = MgO Lined Walls and Top

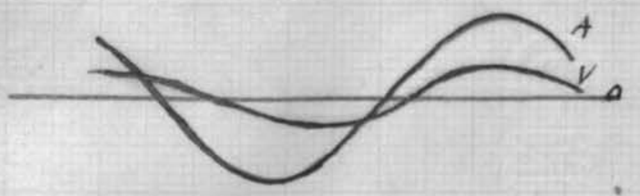
Fig IV
Rectification Test



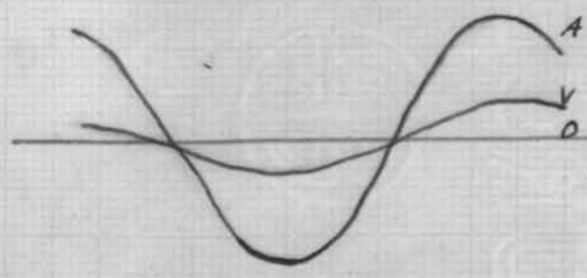
A_1 = A.C. Ammeter
A_2 = D.C. Ammeter
C = Ti_2N_2 Cell
V = Voltmeter
P = Primary coil
S = Secondary coil



At 100 Mill-Amps



At 340 Mill-Amps



At 500 Mill-Amps

Oscillagraph-Curves

A= Amperage Curve
V= Voltage Curve
O= O Line