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Source and Control of Nitride Inclusions in Titanium

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The Bureau of Mines investigated possible sources of nitride defects in the production of magnesium-reduced titanium sponge in order to determine if such defects are capable of surviving consumable electrode arc melting. The production of alpha-stabilized nitride inclusions in hot-rolled titanium plate from air contamination of sponge during its manufacture was experimentally demonstrated. The highest incidence of inclusions in hot-rolled plate resulted from sponge which was reduced by air-contaminated magnesium and from sponge subjected to air contamination during the vacuum distillation cycle and during helium sweep. Maintainance of good vacuum-tight integrity, filtration of molten magnesium prior to charging into the reduction retort, and mechanical attrition of sponge to pulverize and disperse nitrides are suggested as practices to lower inclusion incidence in commercial titanium ingots.

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Source and Control of Nitride Inclusions in Titanium

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SOURCE AND CONTROL OF NITRIDE INCLUSIONS IN TITANIUM

by

Jack L. Henry,[1] S. D. Hill,[2] W. E. Anable,[2] and J. L. Schaller[3]

ABSTRACT

A laboratory and a pilot-plant-scale investigation has been conducted by the Bureau of Mines to examine possible sources of nitride defects in the production of magnesium-reduced titanium sponge. The production of alpha-stabilized nitride inclusions in hot-rolled titanium plate from air contamination of sponge during its manufacture has been experimentally demonstrated.

Magnesium-reduced sponge prepared from air-contaminated magnesium or when contaminated by an air leak during reduction, vacuum distillation, or inert gas sweep, shows very large variations in nitrogen content. Refractory nitrides, delta TiN and epsilon Ti_2N have been identified in this sponge.

The highest incidence of inclusions resulted from sponge that was reduced by air-contaminated magnesium and from sponge subjected to air contamination during the vacuum distillation cycle and during helium sweep.

Air contamination of sponge during the reduction cycle was not nearly as effective in producing inclusions.

Tests showed that color and texture may not be reliable criteria for locating defects during sponge inspection.

Maintenance of good vacuum-tight integrity, filtration of molten magnesium prior to charging into the reduction retort, and mechanical attrition of sponge to pulverize and disperse nitrides are suggested as practices to lower inclusion incidence in commercial titanium ingots.

INTRODUCTION

Void-associated alpha-stabilized defects in titanium ingots is a subject of continuing interest to both titanium producers and aircraft engine manufacturers. The first major incidence of these low-density inclusions (low

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[3] Chemist (now with Boulder City Metallurgy Laboratory, Boulder City, Nev.).

radiographic density) was observed in the late 1950's. It has been stated that 2 to 4 percent of aircraft ingots may contain such defects and that the incidence of defects varies widely with time. This is to say, at times the incidence may be high, but during other significant time intervals few flaws appear.

The nature and characterization of defects in titanium ingots and forged or rolled semifinished products have been described in detail by Fal'kevich (2)[4] and Wood (9). Wood seeded pieces of arc-melted titanium mononitride (TiN) into consumable titanium sponge electrodes and studied both the survival and natures of inclusions after melting. He studied various melting parameters that may have an effect on reducing the incidence of defects. Wood has speculated widely on the subject of possible sources of defects in sponge production, sponge handling, melting and casting, and fabrication. It is stated that many sources probably exist and that certain defects are tied closely to nitrogen contamination.

Fal'kevich studied artificial seeding of consumable sponge electrode with pieces of air-burned sponge having various colors and textures. An inclusion was found in only 1 of approximately 50 5-inch-diameter ingots. This ingot was seeded with burned sponge having a gray-white appearance and containing substantial nitrogen. A total of 15 ingots were seeded with the gray-white sponge. The only one that showed inclusions was made from an electrode in which the burned sponge was placed in drilled holes. He concluded that high-colored sponge pieces are generally low in nitrogen and do not survive melting to become inclusions.

A comprehensive study to define and catagorize the potential causes of inclusions in titanium was also made by Charles F. Krey of Oregon Metallurgical Corp., Albany, Oreg. During his discussion of this unpublished work with the authors, he described the many realistic materials that he seeded into small-scale consumable electrodes, which were vacuum-arc melted to study solution versus survival, and to characterize the resulting defects. These materials included high-nitrogen sponge, AlN, high-nitrogen MIG welds, forge scale, wood chips, and other possible contaminants. He concluded that the contaminant most likely to cause the highest percentage of production alpha defects was high-nitrogen titanium sponge.

During Wood's investigation, a very limited series of tests was made in which nitrogen gas was introduced during the melting of magnesium and at the onset of reduction in the Kroll sponge process. It was observed that nitrogen was transferred to the titanium and that contamination was greatest in the initially formed sponge. This work was in part responsible for the initiation of the larger scale, more extensive investigation reported in this paper.

The objective of this investigation is to contribute to the development of more reliable materials for aircraft construction, to demonstrate experimentally how impurities may be introduced into titanium sponge during

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

manufacture by the magnesium reduction process, and under what conditions they may contribute to the formation of defect-forming impurity clusters and determine how manufacturing methods may be modified to overcome the formation of such defects.

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The authors are grateful to G. G. Thompson, physical science technician, and W. L. Abraham, chemical engineering technician, at the Albany Metallurgy Research Center who operated the sponge pilot plant and contributed greatly to the progress of the project. They also thank the many other staff members for their contributions of mechanical construction and maintenance, ingot casting and forming, metallography, and chemical and physical analyses.

EXPERIMENTAL METHODS

Every attempt was made to make the experimental approach as realistic and practical as possible. A 12-inch-diameter reactor was employed throughout the project. Several methods of air contamination were employed during different stages of reduction and distillation or helium sweep, and the resulting sponge was carefully examined for impurity distribution and possible high-nitrogen defects. The sponge was taken through the consumable electrode melting cycle and through fabrication into plate, which was subsequently examined for defects.

Unfortunately, it was necessary to employ unrealistically high levels of air contamination in order to produce a sufficiently high level of defects to insure their detection.

Titanium Sponge Production

All titanium sponge pilot plant experiments with nitrogen contamination closely simulated the commercial process for sponge manufacture. Magnesium was used exclusively as the reducing metal, and both vacuum distillation and a simulated helium sweep operation were used to remove the excess magnesium and the byproduct magnesium chloride. Although acid leaching is sometimes employed to remove magnesium and magnesium chloride from titanium sponge, nitrogen contamination during this operation was not studied in this project.

Nitrogen contamination was introduced during the sponge production runs by the following methods: (1) nitrided sponge particles were seeded both during the reduction and distillation cycles, (3) air-contaminated magnesium was employed as the reducing metal, (3) both diffuse and localized air leaks were provided during reduction and distillation cycles, and (4) continuous air leaks were designed into the helium stream to simulate a contaminated inert gas sweep operation.

Materials

The titanium tetrachloride ($TiCl_4$) used in this study was procured from a major titanium sponge producer. It was obtained in 55-gallon drums and transferred directly to the reduction assembly metering tank prior to each pilot plant run. Primary magnesium employed was in the form of ingots that conformed to the requirements of the American Society for Testing and Materials (ASTM) Designation B92-66. Typical impurity analysis of the primary magnesium and the titanium tetrachlorides used in this study are shown in table 1.

TABLE 1. - Materials impurity analysis, ppm

Element	$TiCl_4$ analysis	Magnesium analysis
N	-	8- 18
C	-	30-203
Al	<10	20- 30
B	-	<5- 10
Ca	<10	<10
Cd	-	<5
Co	-	<5
Cr	<10	<10- 10
Cu	<10	15-100
Fe	<10	<10- 10
Mn	<50	<10- 30
Mo	<15	<10
Ni	<20	<5- 20
Pb	<100	20- 30
Si	<30	20-300
Sn	<100	<10- 30
Ti	-	<10- 20
V	<40	<10- 20
Zr	-	500

Air used in the air contamination experiments was supplied from a pressurized cyclinder of hygienically pure air. This air was employed in order to avoid possible water and oil contamination that might result if impure compressed air was used. The air in these Air-Pak[5] cyclinders was supplied by a major supplier and had a reported analysis of less than 5 ppm methane, no detectable oil vapor, no detectable CO_2, and water concentration equivalent to -185° F due point.

Equipment and Procedure

Figure 1 shows a schematic diagram of the 12-inch-diameter reduction and distillation systems used in the sponge production studies. Figure 2 is a photograph of an overall view of the pilot plant. Both furnaces were of the electric resistance type. Retorts, shields, baffles, salt receiver, and titanium tetrachloride metering tank were all constructed from stainless steel. In addition, stainless steel was used for all liquid transfer lines, gas bleed lines, valves, and thermocouple sheaths.

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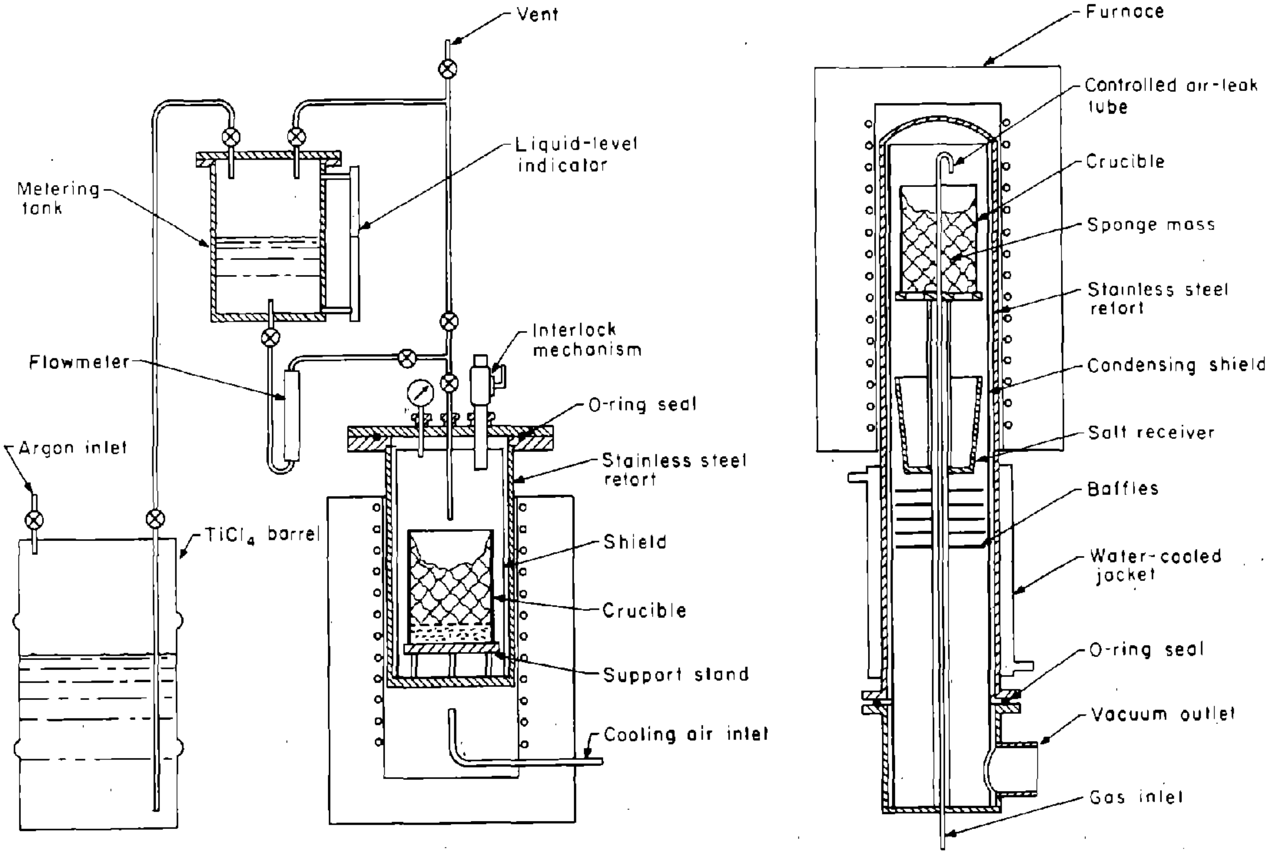
[5] Reference to specific manufacturers and brands is made to facilitate understanding and does not imply endorsement of such manufacturers and brands by the Bureau of Mines.



Reduction

Distillation

FIGURE 1. - Schematic diagram of titanium sponge pilot plant.

Initially, the crucibles were about 12 inches in diameter and 16 inches high and were constructed from 16-gage mild steel. Utilization of mild steel crucibles resulted in some iron contamination of the titanium sponge, therefore CP-titanium sheet, 0.065 inch thick, was used to make crucibles. When mild steel crucibles were being used, they were used only once and then cut apart to remove the sponge. The titanium crucibles were reused five to six times; after each run, they were cleaned and sandblasted.

Magnesium ingots were prepared for use by pickling in dilute hydrochloric acid to remove oxide scale from the surface. After removal from the acid bath, the ingots were washed in cold running water, dried with a clean cloth, weighed, and placed in a clean, freshly sandblasted crucible. After 20 pounds of magnesium pig was loaded into a reduction crucible, the crucible was placed in the reduction retort along with a clean, dry, stainless steel shield. The lid was then put in place and sealed. After sealing the main flange, the entire retort system was placed in position in the furnace, and the thermocouples, attached to the surface of the retort, were connected. The titanium tetrachloride feed line, gas bleed line, the pressure-vacuum gage, and interlock mechanism or controlled air leak mechanism were then attached using vacuum quick-disconnects, and the entire system was evacuated to 50 micrometers and then backfilled with helium to 5 psig pressure.

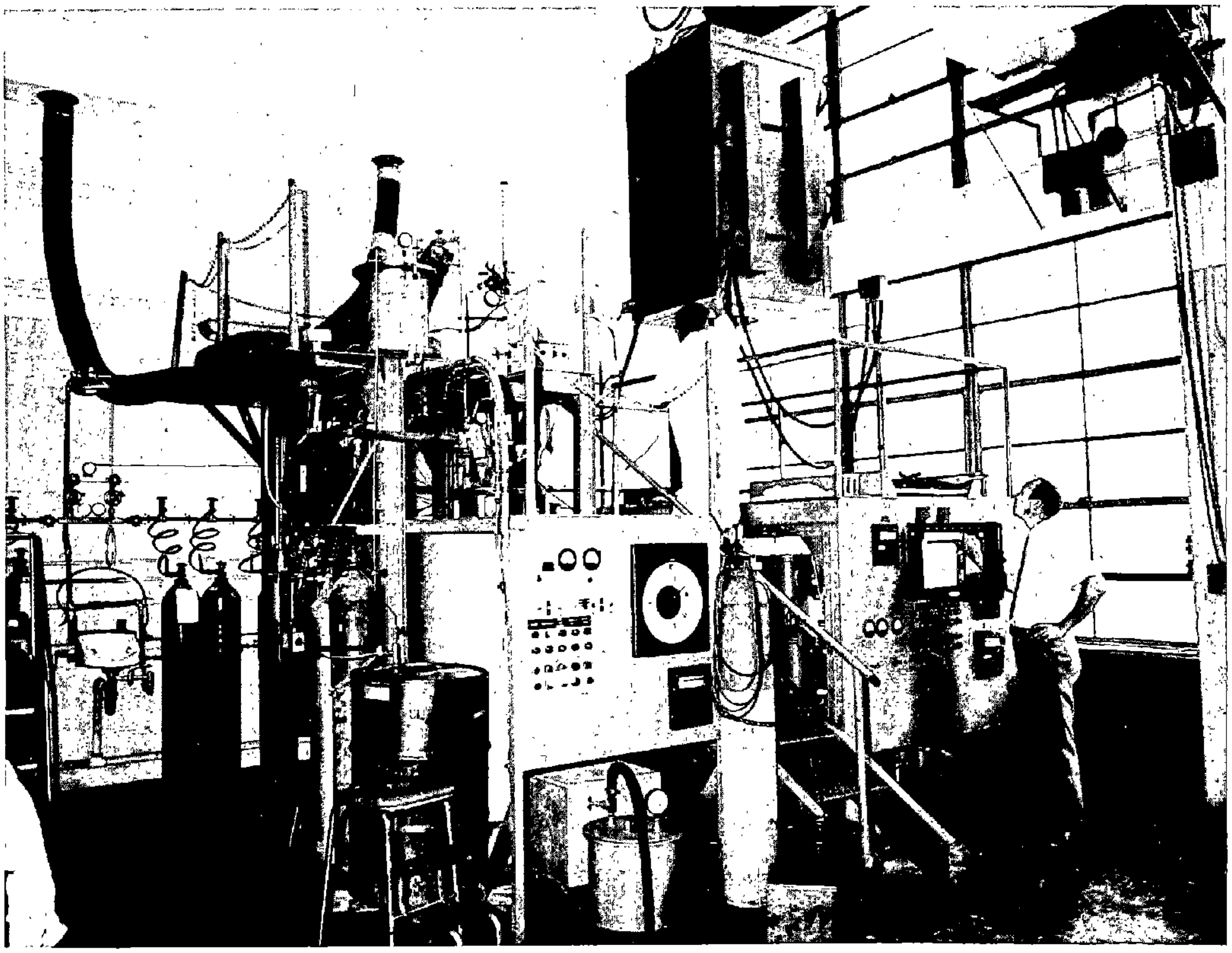


FIGURE 2. - Titanium sponge pilot plant.

The titanium tetrachloride metering tank was filled prior to each run by slightly pressurizing the 55-gallon drum with inert gas pressure and forcing the liquid to flow up to the metering tank. The metering tank was equipped with an indexed liquid-level indicator that was calibrated in pounds of $TiCl_4$. The tank held approximately 100 pounds of liquid $TiCl_4$.

To establish a balanced pressure in the reaction chamber prior to melting the magnesium, the valve connecting the retort with the top of the metering tank was opened. The power was then turned on and the furnace temperature brought up to 850° C, as indicated by the three thermocouples located on the outside of the retort. The temperature was held at 850° C for about 1 hour while the magnesium completely melted. In some of the early runs, a sight glass was attached to the main flange and the magnesium melting could be observed.

When the magnesium was completely molten, the $TiCl_4$ was allowed to flow by gravity from the metering tank into the crucible at a rate of about 1 pound per minute. Since the reaction was exothermic, the power to the furnace was cut off when the reaction was initiated, and cooling air was blown over the retort in order to maintain the temperature between 750° to 850° C during the entire reduction period. Most reduction runs were stopped after 50 to 60 pounds of $TiCl_4$ had been added. This procedure resulted in a magnesium utilization of 60 to 75 percent and prevented the formation of excessive amounts of lower chlorides of titanium. Details of the titanium reduction reaction and characteristics of the metallic titanium sponge that is formed have previously been described by several authors (4, 6, 8).

After the reduction cycle was complete, the system was cooled overnight while maintaining a helium pressure of 5 psig in the crucible. The crucible containing the titanium sponge mass, excess magnesium, and reaction product magnesium chloride was then removed from the reduction retort. As rapidly as possible, several 1/4-inch holes were drilled in the bottom of the crucible, and it was placed on the pedestal of the distillation retort assembly. When the reaction mass was heated, under vacuum, to the melting point of the salt in the distillation retort, most of the salt would run out of the sponge mass and into the salt can located below. The remainder of the salt and excess magnesium was vacuum distilled out of the sponge mass. The distillation was carried out at a tempeature of about 925° C for 30 hours. A pressure of less than 0.1 torr was maintained at all times, and at the end of the cycle, the pressure was usually on the order of 10^{-4} torr. After distillation, the retort was cooled overnight, and the sponge was passivated at room temperature by backfilling to 1 atmosphere with pure argon and holding for 1 hour, then pumping down and repeating the operation with a mixture of 20 percent oxygen in argon.

When both the reduction and distillation cycles were completed, the complete assemblies including retorts, shields, baffles, etc., were cleaned in dilute hydrochloric acid, rinsed with flowing cold water and placed in a large chest-type drying oven where they remained until ready for another run.

The 1/4-inch holes in the titanium crucible were welded closed so that the crucible could be reused.

During the first two experiments, the crucible was placed in the distillation retort in an inverted position. Molten magnesium that ran out reacted with titanium subchloride on the upper crucible walls producing a very fine dendritic sponge. This was very difficult to sample, so the technique was discontinued.

Nitrogen-Contamination Procedure

All of the pilot plant sponge production runs, with the exception of the control runs made to develop operating procedures, were made to study the production of nitrogen defects in the sponge by introducing nitrogen. Initially, nitrogen defects were introduced by the addition of approximately 1-gram pieces of air-burned sponge, nitrided sponge pieces, or magnesium nitride pellets into the reduction crucible at various stages during the reduction cycle. These defect pieces were introduced through a vacuum-lock mechanism located on the main flange of the reduction retort system shown in figure 1.

A second method was to add a controlled amount of air prior to introducing the $TiCl_4$. This air reacted with the molten magnesium and formed a magnesium-nitride, magnesium-oxide dross on the surface of the metal. The amount of air allowed to react with the molten magnesium was based on the pressure, volume, and temperature of the system. The amount of oxide and nitride dross was calculated from the observed pressure change.

A third method of accomplishing nitrogen contamination during the sponge manufacture was to introduce a controlled amount of air as an air leak, either diffuse or localized, during either the reduction or distillation cycle. The diffuse air leak during reduction was accomplished by flowing a controlled amount of air continuously into the top portion of the reduction retort during the entire reduction period. The titanium sponge pilot plant used in this study is shown in the schematic diagram in figure 1 and in the photograph in figure 2.

Before proceeding with the localized air leak experiments, a series of tests was made to determine the most realistic and best site for the localized air leak. In this series, runs were made in which the $TiCl_4$ additions were terminated prematurely to simulate partial consumption of the available magnesium; that is, 10-, 20-, 40-, and 50-percent reduction. After the reaction mass had cooled to room temperature, the crucible was removed from the retort and cut in half so the location of the salt, excess magnesium and sponge formation could be observed. After photographing these sponge deposits, one half was water leached to remove only the salt. The other half was vacuum

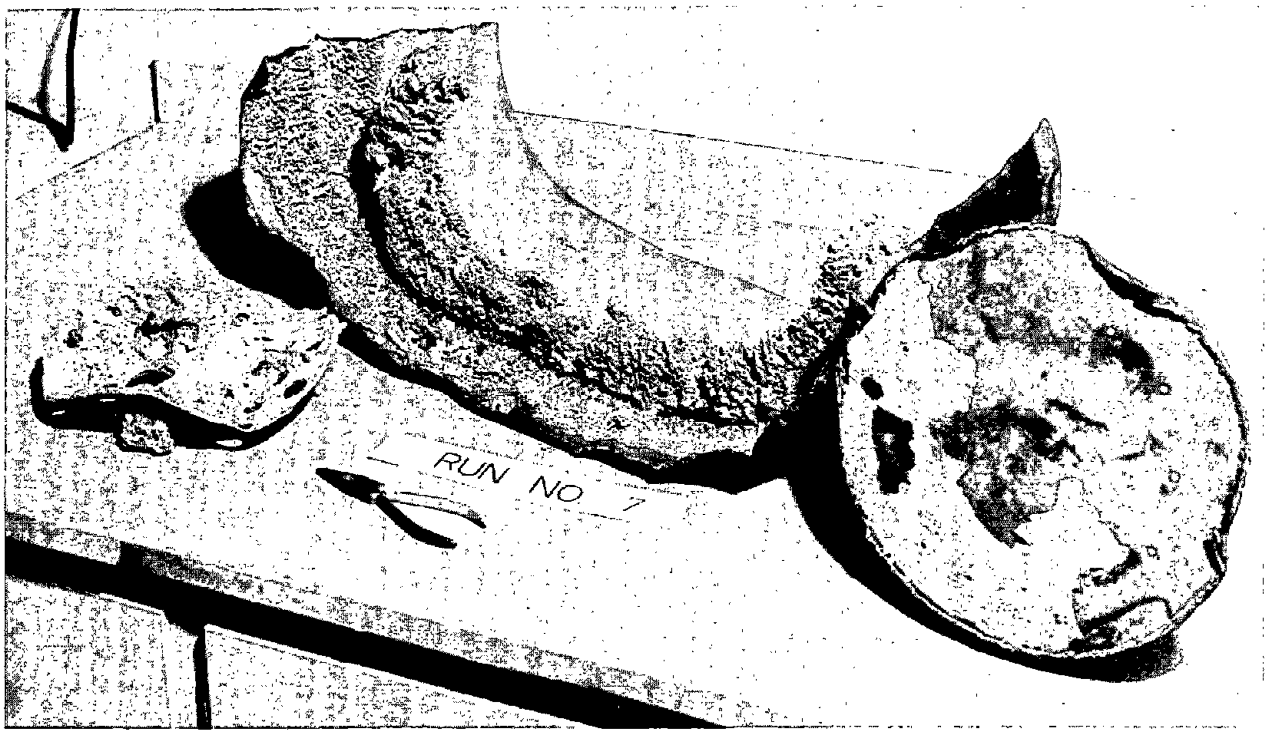


FIGURE 3. - Sponge from a 22-percent reduction run.

distilled to remove both the salt and excess magnesium. Figure 3 shows one such run in which only 22 percent of the magnesium was used. Note the initial formation of sponge on the crucible wall where the leak should be located. Using the information gained from this series of tests, localized air leak experiments were conducted by locating a 1/4-inch titanium tube in the desired location (1 inch from the sidewall and 6 inches from the bottom) within the crucible and continuously introducing a controlled air leak through this tube during the entire reduction period.

Both diffuse and localized air leaks were also effected during the distillation cycle of the sponge production. Diffuse air leaks were accomplished by continuously introducing a known amount of air through a 1/4-inch titanium tube with the outlet located about 6 inches above the surface of the sponge mass, as illustrated in figure 1. Localized air leaks were conducted by locating the outlet of the tube in the heart or center of the sponge mass and again flowing air continuously at a controlled rate during the entire vacuum distillation cycle. Figure 4 illustrates how the localized air leak was accomplished during the distillation cycle.

One other method of introducing air was to include the controlled air leak with the helium when simulating the helium sweep operation. The

FIGURE 4. Sponge contaminated by air led in through titanium tube during distillation cycle.

procedure used for these tests was to melt out and vacuum distill the salt from the sponge mass for about 30 hours, then backfill the system with helium to atmospheric pressure while still at temperature and continuously purge the system with helium mixed with a known amount of air for 4 to 8 hours. The total amount of air introduced during this 4- to 8-hour period was comparable with the total air introduced during the 30 hours of distillation for the air-leak vacuum distillation runs.

Titanium Sponge Evaluation

The appearance and physical properties of the precursors of high-nitrogen inclusions that might be found in titanium sponge were not known. Therefore, a study was undertaken. It included preparing artificial defects and the seeding these defects into titanium sponge, both during the reduction process and immediately prior to the distillation step.

Distribution of impurities in contaminated titanium sponge is very uneven, and sampling techniques that involve melting or severe mechanical working of the sponge result in changing the interstitial impurity levels. Analytical procedures currently in use by the analytical chemistry laboratory were satisfactory for use on this project, but methods of sampling the sponge had to be developed.

A number of potential methods of locating precursors of high-nitrogen defects in the sponge mass were investigated.

Sampling for Analysis

The geometry of the sponge cake to be examined varied somewhat from run-to-run owing to variations in the conditions of the reduction, which could not be completely controlled. However, in most cases the sponge cake could be divided into regions that were comparable with respect to the type of sponge and locations in the crucible. A typical sponge batch is shown in figure 5. The crucible was cut away and the sponge mass was placed with the top surface visible. The perforated plate on the crucible bottom was used to support the sponge cake.

As a rule, the sponge cake was separated into seven or eight regions that were sampled for analysis. Considerable differences existed in the appearance, hardness, and ductility of the sponge from various regions. A typical selection of regions is as follows:

1. A dense sintered mass resembling dried mud on the bottom of the plate. This was usually separated completely from the main mass of sponge.

2. An oval or pear shaped ring of corallike sponge just above the bottom plate. This was usually attached to the central mass by buttresslike arms.

3. A dendritic sponge growing from the crucible sides toward, and frequently connected to, the central mass.

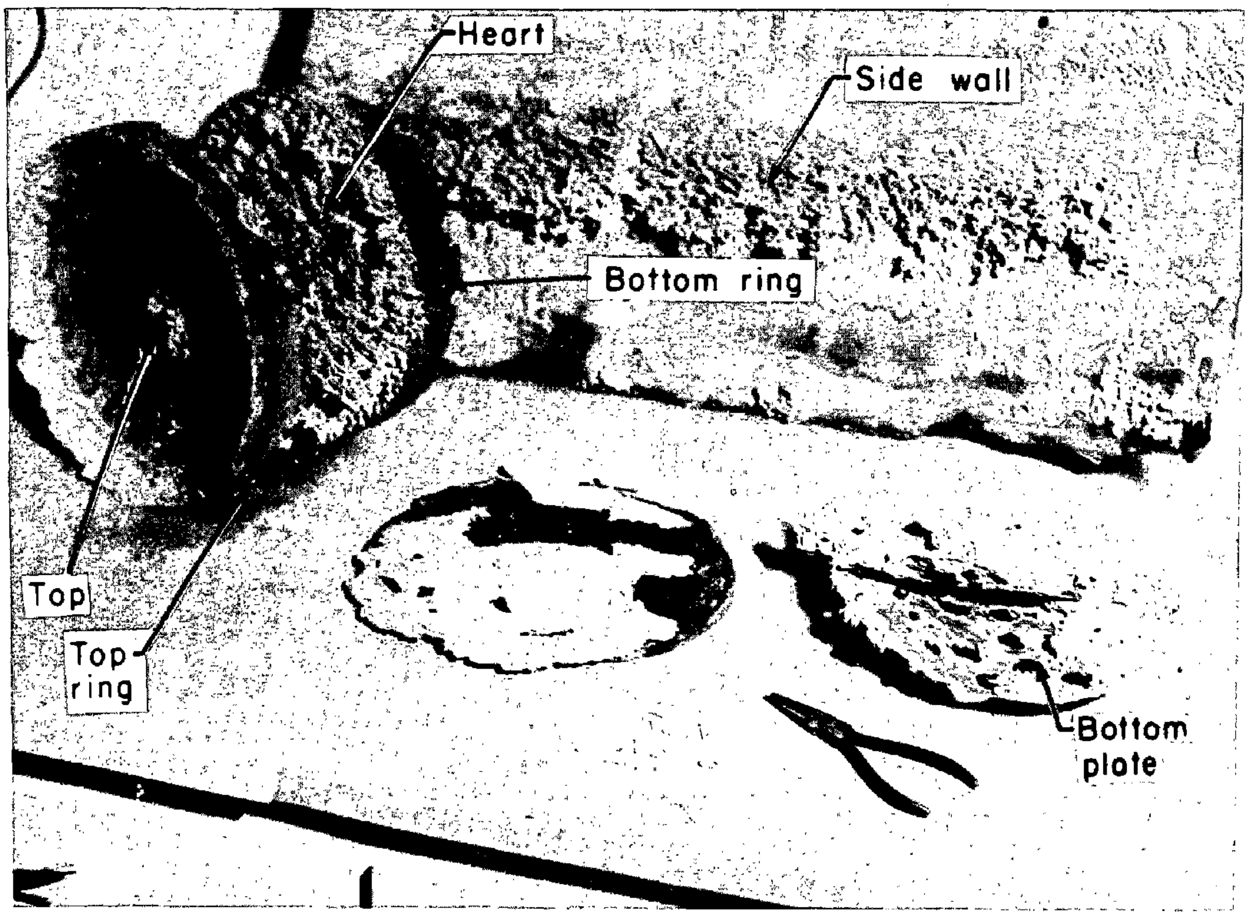


FIGURE 5. - A typical sponge cake with crucible cut away.

4. A very dense, heart-shaped mass of sponge, centrally located and growing down from the top of the cake. The bottom two-thirds of this heart was usually surrounded by a dendritic sponge.

5. The upper third of this heart, usually surrounded by a mixture of laminated and honeycomblike sponge and extending as a layer of decreasing thickness until connecting with a denser wedge-shaped ring structure attached to the crucible wall.

6. A soft feltlike layer of crystalline sponge covering most of the top.

7. A thin layer of sponge covering the crucible bottom and upper sidewall. This was usually not sampled, but occasionally, a significant quantity of dendritic sponge formed on the sidewall above the top layer.

8. The fifth and sixth layers were not present in a few runs.

Obtaining a representative sample from a mass of titanium sponge is quite difficult. The most common procedure has been to sample an arc-melted ingot or a button melted from a large sponge sample. This procedure is impractical when the object of the study is to determine the distribution of impurities in the sponge cake, and to determine the impurity levels of the sponge before melting. The initial impurity level may be raised in an unpredictable way be the melting process.

Briquetting the sponge and taking samples by filing, drilling, or machining was tried, but the buildup of heat by mechanical working of pressed sponge results in a prohibitive buildup of impurities. Therefore, the sponge was sampled manually; it was broken down with hammer, chisel, and pliers to 1/4- to 1/2-inch size, and then repeatedly split and further broken down until a 10-gram sample was obtained. The sample was finally broken down to minus 20 mesh.

Analyses

Analyses performed on sponge samples included quantitative determinations of O, N, C, H, and Cl, as well as the semiquantitative analysis of metallic impurities. Particular samples were examined by X-ray diffraction and/or electron microprobe. Oxygen was determined by inert gas fusion techniques using chromatographic determination of CO_2. Carbon was determined by induction heating ignition with chromatographic determination of CO_2. Nitrogen was determined by semimicro-Kjeldahl analysis. Hydrogen was determined by hot extraction and chromatographic determination of H_2. Chlorine was determined by dissolution in nitric acid followed by oxidation with hydrogen peroxide and a potentiometric titration with $AgNO_3$.

Semiquantitative analyses of metallic impurities were run by dissolution of the sample in sulfuric acid, drying and igniting, pelletizing with carbon and analyzing the spectra from a high-voltage spark. The spectra was recorded on a photographic plate and compared visually with a standard spectra.

Attempts to Locate High-Nitrogen Defects in Sponge

Samples of nitrided and air-burned sponge were prepared from pure titanium sponge. Both Japanese sponge and sponge made by a domestic producer were used.

Sponge particles were nitrided by suspending them from a Cahn electrobalance in a nitrogen atmosphere at 800° to 900° C. Small pieces of titanium sponge were ignited with an oxy-hydrogen torch. Typically, the sponge piece would glow locally, then flare up to a white heat and burn out. The more completely burned pieces were covered with a grayish or yellowish slag, which appeared to be fused rutile, but proved to be high in nitrogen. The burned sponge, exclusive of the slag, varied greatly in color. The burned sponge also had high gradients in nitrogen content.

Both nitrided and burned sponge were seeded through a vacuum lock into the reduction retort at intervals during the reduction. Both types of synthetic defects were also placed in the reduction crucible before the start of the distillation cycle.

Defects seeded during the reduction cycle were located by dissection of the sponge to 1/4- to 1/2-inch pieces. The defects were more brittle than the main body of the sponge and sometimes showed a different appearance than the host sponge.

Sponge briquets were seeded with nitrided sponge, air-burned sponge, and also arc melted TiN. Generally the seeds were placed in the sponge as the press was charged, but it was thought that some seeds might be crushed during the pressing at 40 tons per square inch: therefore, some seeds were placed in holes drilled in the briquets. The seed locations were charted, the briquets were clad in 3/8-inch mild steel and hot-rolled at 850° C to 75-percent reduction, stripped, and in some cases cold rolled further. The surface of the rolled sheet showed evidence of inclusions only in the case of an arc-melted TiN fragment that broke through. Some inclusions were found by sectioning the sheet, often in the form of small groups of fragments which indicates that the inclusions broke up during processing. Attempts to detect the inclusions by cobalt-60 radiography were unsuccessful.

Several bars were subjected to ultrasonic testing. No significant scan breaks could be definitely correlated with inclusions.

Since hydrided titanium may be easily reduced to a fine powder, a number of tests were made to determine if nitrided titanium would resist hydriding and retain enough strength that the sponge could be hydrided and reduced to powder and screened to separate the high-nitrogen defects.

Titanium sponge, nitrided titanium sponge, and high-nitrogen arc-melted compositions were hydrided at 1 atmosphere and 500° C. Although an arc-melted composition ranging from 11 to 20 percent by weight of nitrogen did not hydride at temperatures up to 700° C, sponge samples containing up to 5.71 percent nitrogen hydrided easily and were easily reduced to a fine powder. Natural defect pieces obtained from a commercial titanium producer also proved very friable. It was concluded that differences in friability of the hydride could not be used as a means of separating defective sponge pieces from normal sponge.

A number of tests were made to determine if normal sponge and high-nitrogen sponge could be separated by their chlorination behavior. Tests were made on natural sponge and sponge nitrided to 6.13 weight-percent nitrogen. Both 100 percent chlorine and 10 percent chlorine - 90 percent argon mixtures were used. The temperature at the onset of chlorination was between 250° and 300° C. Both materials chlorinated, leaving very little residue. The observed difference in reaction rate and temperature onset of chlorination were not large enough for a practical separation.

The special emissivity of pure titanium is 0.63 and that of pure TiN is 0.79 to 0.82 at 65-micrometer wave length; TiO_2 has an emissivity coefficient of 0.50 on a titanium surface. Tests were conducted to determine if high-nitrogen particles could be distinguished from normal sponge by the difference in its reflectivity in infrared light. Twenty-three specimens of different types of titanium sponge, natural defects, nitrided sponge, and button-melted TiN were photographed with infrared film. Photographs were taken using stroboscopic light, photoflood light, and infrared light; no significant differences were noted.

Ingot Melting, Fabrication, and Evaluation

It became apparent after about 6 months that locating high-nitrogen defects in sponge by inspection methods was not dependable. It also became apparent that even if high-nitrogen fragments were found, they may not survive a single or a double arc-melting operation. For these reasons, it was decided to carry the test sponge through one or two melting cycles and fabricate the ingot into plate for inspection. This approach appeared to be the most practical.

Electrode Preparation

All control lots and air-contaminated lots of titanium sponge to be fabricated into plate were first mechanically broken down into 1- to 2-inch pieces by hand tools. All regions of the sponge cake were retained. The sponge pieces, together with any residual powder from the mechanical attrition, were thoroughly mixed and pressed at 40 tons per square inch into electrodes measuring 2 by 1 by 10 inches. (See figure 6.) Approximately three such bars from each sponge lot were arc-welded end-to-end in a pure helium atmosphere to produce a consumable electrode.

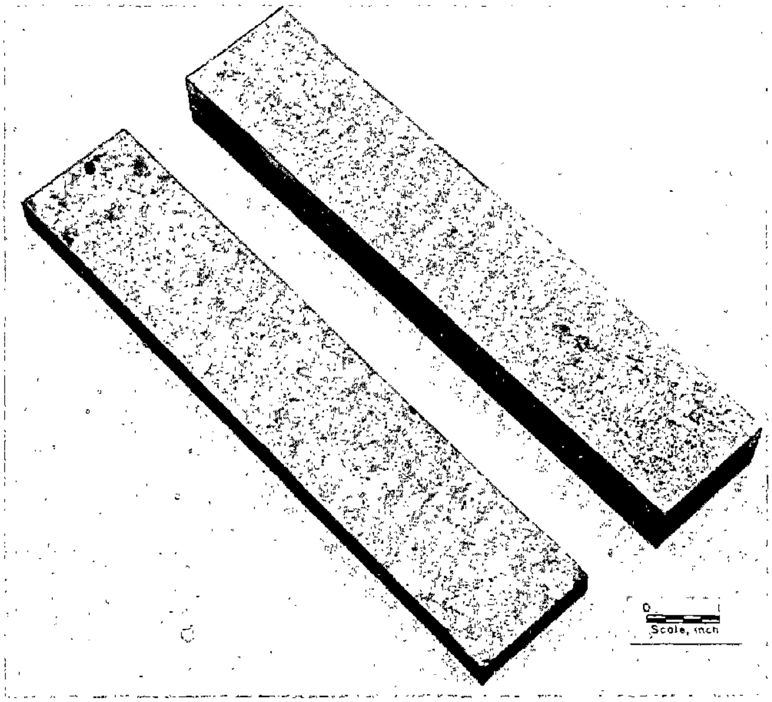


FIGURE 6. - Typical titanium sponge briquets for use as consumable electrodes.

Ingot Melting

The electrode was placed in an 8-inch-diameter consumable-electrode-arc furnace, and the system was evacuated to 0.01 to 0.04 torr. Approximately 200 grams of unpressed sponge of the same lot was placed in the 3-1/2-inch-diameter water-cooled crucible to act as a base for melting. Melting was usually started at about 1,500 amperes and 25 volts; this was soon raised to about 3,000 amperes and 30 volts. Direct current was used in all melts with the polarity of the consumable electrode negative.

After removal from the crucible, the ingot was placed in a lathe where the crown was removed and the

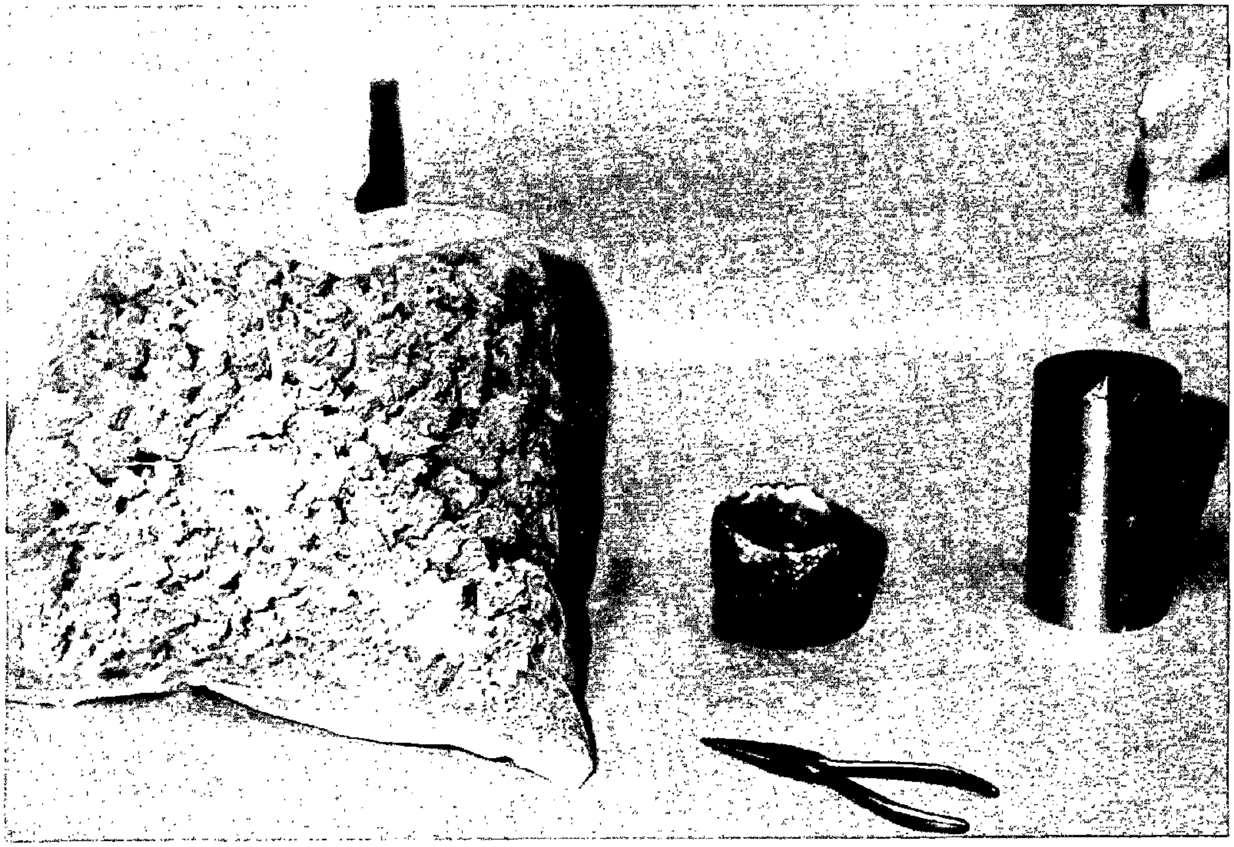


FIGURE 7. - Typical sponge prior to briquetting; crown of ingot and machined ingot ready for hot-working.

sidewalls and bottom machined to prepare the ingot for hot working. Figure 7 shows the sponge before pressing, the removed crown, and a machined ingot prior to hot working.

Hot-Working

The machined ingot was heated in air to 1,120° C and upset at least 50 percent in a forge press. A considerable amount of redundant work was put into the shorter ingots. The billet was then hot-rolled at 980° C at right angles to the direction of forging to 3/4 or to 1/2 inch in thickness. The plate was then beta-annealed at 1,120° C for 30 minutes, water quenched, sandblasted, and surface-ground in preparation for inspection. The finished plate usually represented about 60 percent of the total original sponge.

Plate Inspection for Nitride Inclusions

The first 13 of over 50 fabricated titanium plates produced in this project were ultrasonically inspected in an attempt to locate possible inclusions. Ultrasonic scanning was done at 5 megahertz with the plate submerged in water. Water path from lithium sulfate crystal to plate surface was 3 inches. A standard, having flat-bottom holes 0.020, 0.030, 0.040 inch in diameter, was employed at the beginning and end of each plate scan. In all cases, the standard holes showed distinct scan breaks.

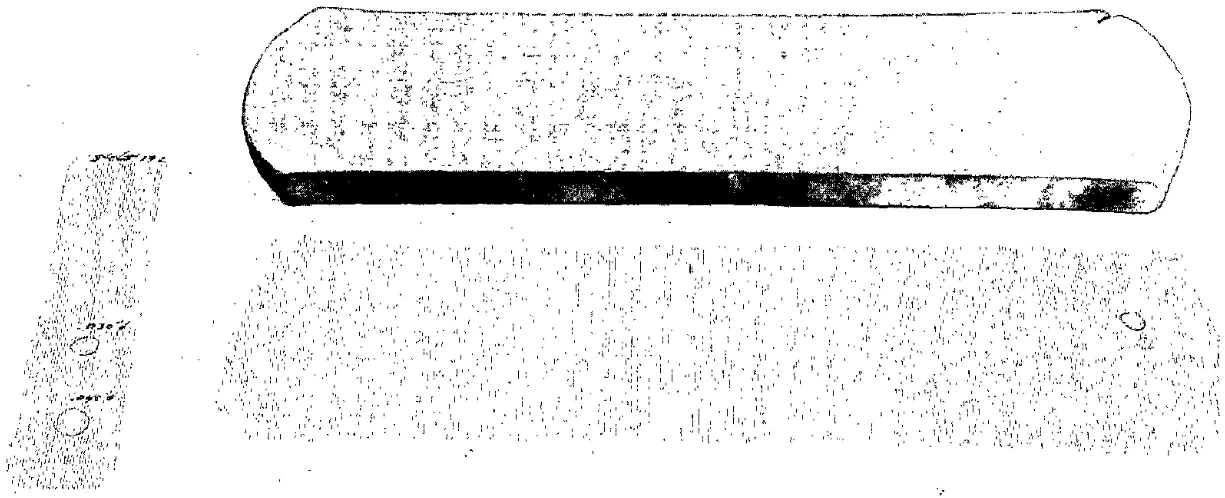


FIGURE 8. - Titanium hot-rolled plate and sonic chart.

Although scan breaks were usually seen on the charts for the titanium plates, the correlation between scan breaks and high-nitrogen inclusions was very poor. Because of the poor correlation, sonic testing was discontinued. A typical plate and sonic chart are shown in figure 8.

All plates were inspected for inclusions by making cuts through the plate at right angles to the longitudinal axis at 1-inch to 1/2-inch intervals. The cuts were made with an abrasive cutoff wheel (Allison C120-JRA 2,200-rpm wheels). The exposed surface produced was then carefully examined for inclusions, first by unaided eye and then by binocular microscope from 6 to 50 power. Nitride inclusions, if present, are easily seen on the surface cut by an abrasive cutoff wheel without further machining or sanding. If no inclusions were observed, additional internal area was exposed by machining on a shaper, taking 0.005-inch cuts. Occasionally, a belt sander was used to expose additional internal area. Figure 9 shows two partially dissected plates.

Nitride Inclusion Evaluation

If nitride inclusions were located in a titanium plate, it is possible to express their frequency, size range, and physical and chemical characteristics at least in a semiquantitative manner. The big problem arises when inclusions are not observed. It is not possible to state that the sponge lot was free of inclusion-forming nitride defects. Since about 40 percent of the metal is lost in the processing of sponge to plate, even if the plate were free of inclusions, one or more defects could have existed in the metal lost during melting, machining, and fabrications.

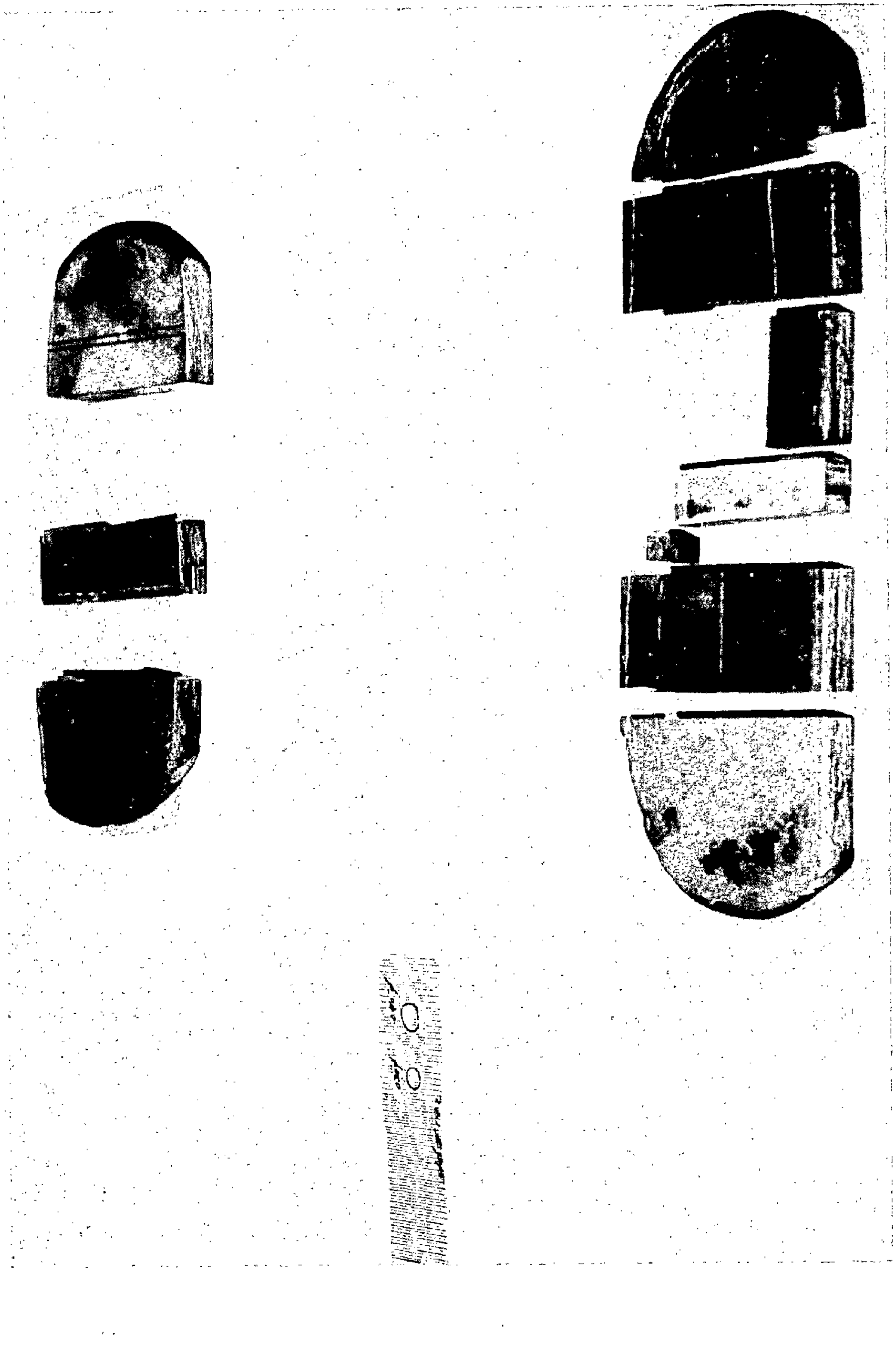


FIGURE 9. - Partially dissected titanium plates and sonic charts.

Inclusion Incidence

An attempt was made to express the inclusion frequency in a semiquantitative manner so that a rough comparison could be made between methods of air contamination employed. The term "inclusion index" is defined as the number of inclusions, 0.1 millimeter or greater in diameter, per cubic centimeter of metal inspected by cutting and machining. Whenever inclusions were observed on the surfaces exposed by cutting the plates with an abrasive wheel, each surface was assumed to represent a volume composed of the product of the surface area and a depth equal to the diameter of the smallest inclusion considered. If inclusions were not observed on the original surfaces, additional metal volume was examined by taking 0.005-inch cuts on a shaper. The volume thus estimated is used to compute the intensity, as inclusions per cubic centimeter, and the volume-percentage of the titanium plate inspected.

Inclusion Identification and Characterization

Suspect inclusions on the exposed surface of the titanium plates were examined with the unaided eye and then by binocular microscope at 6 to 50 power. In many cases real nitride inclusions are associated with a comet tail made by the brittle material crumbling out and scratching the titanium surface during the cutting operation. A simple scratch test using a steel scribe can often be used to screen out artifacts from true nitride inclusions.

In all cases, however, two or three typical inclusions were micropolished and etched with nitric acid-hydrofluoric acid-water etchant and examined for structural characteristics. These samples were then inspected by electron microprobe for nitrogen and oxygen content to confirm that they are genuine nitride inclusions.

Molten Magnesium Filtration

It was considered possible that nitride defects in sponge may originate from impurities in the magnesium.

Fortunately the solubilities of $MgCl_2$, MgO, and Mg_3N_2 in liquid magnesium (1) do not exceed 10, 50, and 50 ppm respectively; therefore, tests were made to remove excess quantities of these constituents by passing the molten metal through a steel wool filter. Shown schematically in figure 10 is the apparatus used for melting magnesium in a controlled atmosphere, adding known amounts of air to form a dross (Mg_3N_2 and MgO), and for removing the dross (filtering) and collecting the clean metal. The basic system includes a 4-inch-ID chamber 30 inches long surrounded by an electric heater capable of raising the temperature to 900° C. The lower plate was threaded to receive a 1/2-inch pipe, which acted as a valve to contain the molten magnesium. Below the valve, a steel wool filter was installed to remove the dross as the contaminated metal passed by gravity to the collection vessel (reduction crucible). About 50 grams of size 0 steel wool was used to form a filter pad 4 inches in diameter by 3 inches in thickness.

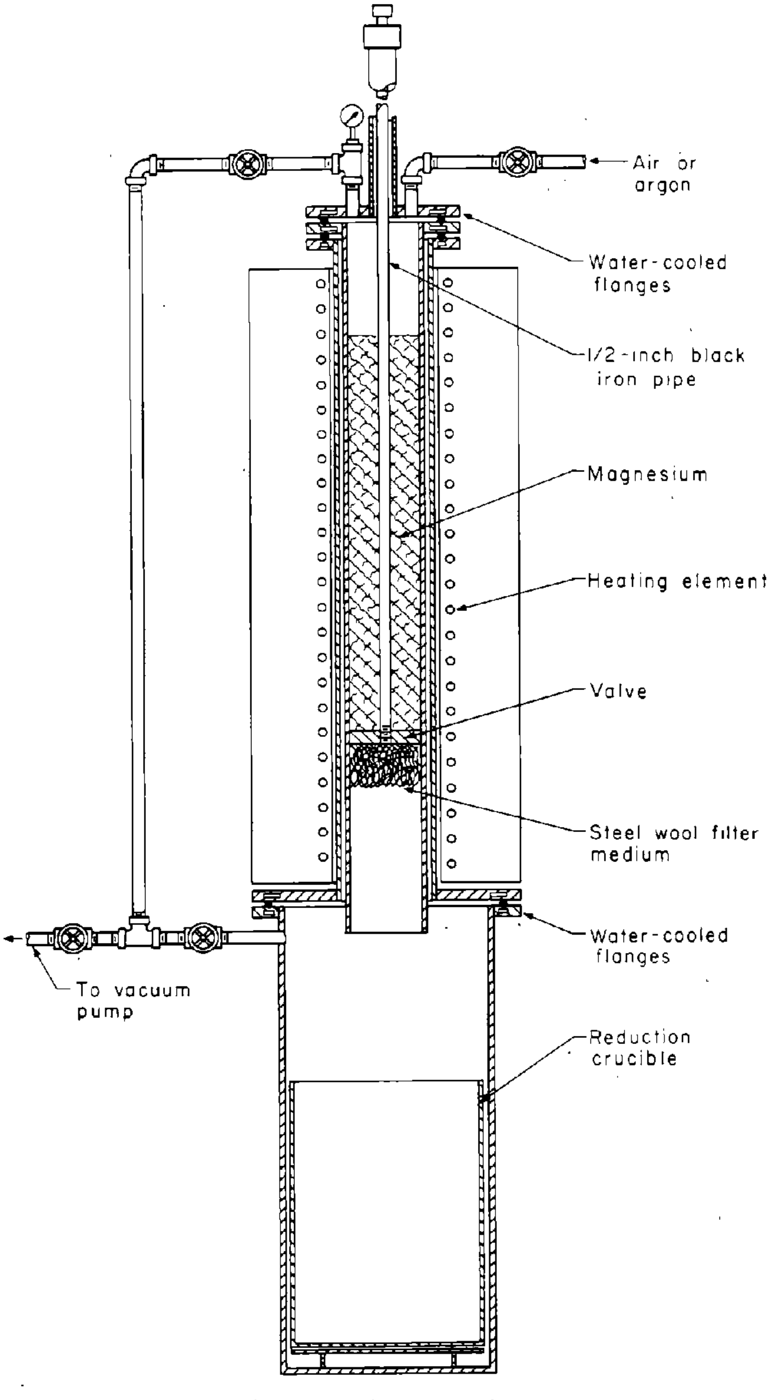


FIGURE 10. - Schematic diagram of molten magnesium filter system.

The chamber for melting magnesium and the reduction crucible were contained in a vacuum chamber, the flanges of which were water cooled to protect the rubber O-rings. Appropriate piping was also included as shown in figure 10 to evacuate the system, and to backfill the upper and lower chambers with air or argon. Provisions were made to introduce known quantities of air to contaminate the molten magnesium and form a dross.

In practice about 6 pounds of magnesium was loaded into the chamber, and the system was closed and evacuated to about 30 micrometers for 24 hours. Argon was then introduced to 5 psig and the magnesium melted. Argon was vented and air introduced to supply 60 grams of nitrogen per 20 pounds of magnesium. Once the desired dross was formed, the valve was opened and the contaminated magnesium was allowed to pass through the filter and collect in the crucible below. The crucible was then cooled to room temperature, quickly transferred to the Kroll reactor, and this charge employed to reduce $TiCl_4$ to a batch of titanium.

Mechanical Attrition of Sponge

Charles F. Krey of Oregon Metallurgical Corp., Albany, Oreg. discussed with the authors his unpublished work on high-speed impact crushing of titanium sponge to reduce the size of hard particles, which could be a source of inclusions. He postulated that this treatment might lead to a lower incidence of inclusions in double-melted ingots and encouraged us to further examine the idea.

In this study, a high-energy mill was used to comminute sponge and dislodge the harder friable particles from the softer ductile sponge. A 16- by 16-inch hammer mill equipped with a 20-horsepower drive (1,750 rpm) was available for these tests. The mill was equipped with a grate having 1/2- by 4-inch openings oriented perpendicular to the direction of hammer rotation. Argon was used to flush air out of the mill prior to use, and a steady flow was maintained during the milling operations. Broken sponge, measuring 1 to 2 inches on a side, was fed piece-by-piece to limit the possiblity of igniting sponge within the mill. The discharge pan was also emptied at frequent intervals to prevent accumulation of sponge that might ignite in event of fire.

Two types of contaminated sponge were subjected to this treatment: (1) Sponge prepared from air-oxidized magnesium, and (2) sponge subjected to a diffuse air leak during distillation. Sponge from each lot was crushed, sized, and divided into two equal portions; one was melted as-received and from the second lot the minus 20-mesh material was removed before pressing and melting the electrode.

EXPERIMENTAL RESULTS

Control Runs

At the beginning of the program, several control lots of sponge were produced to optimize the equipment and the procedure and to determine the quality of the product and the impurity distribution in the sponge cake. Data on impurity levels in four arbitrary regions of the sponge cakes are presented in table 2. The bottom region contains the highest impurity level, as would be expected because this first sponge formed tends to getter impurities in the system. Chlorine and magnesium levels tend to run high, but may be reduced by longer distillation time. Iron, which has not been listed in the table, was usually over 5,000 ppm when a mild steel crucible was employed. Because of this, pure titanium crucibles were employed during most of the study.

Since the study was concerned with nitrogen contamination, it was particularly reassuring to find the nitrogen content of the control runs to be very low.

TABLE 2. - Purity summary of control sponge lots, ppm

	Region of sponge cake			
	Top	Heart	Wall	Bottom
Oxygen (8 lots):				
Maximum...............	1,190	1,600	1,770	3,200
Minimum...............	433	235	443	400
Average...............	851	802	1,058	1,438
Nitrogen[1] (7 lots):				
Maximum...............	94	114	144	255
Minimum...............	9	12	10	44
Average...............	37	52	62	139
Carbon (13 lots):				
Maximum...............	1,588	504	1,684	2,755
Minimum...............	118	84	99	169
Average...............	447	293	512	679
Chlorine (13 lots):				
Maximum...............	2,770	2,330	3,180	2,680
Minimum...............	240	400	410	430
Average...............	1,331	909	1,447	1,554
Magnesium (13 lots):				
Maximum...............	2,000	5,000	5,000	5,000
Minimum...............	100	100	200	800
Average...............	623	1,946	2,328	3,192

[1] None of the seven lots subjected to deliberate nitrogen or air contaimination.

Two lots of sponge were melted and the ingots fabricated to 3/4-inch plate for inspection. No inclusions were found. Data are given in table 3, runs 15 and 35.

TABLE 3. - Effect of air-contamination method and level of sponge on the incidence of nitride inclusions in hot-rolled plate

Run No.	Sponge treatment	N_2 added as air, ppm[3]	Nitrogen in plate, ppm	Nitrogen retention, pct	Inclusions found per cubic centimeter	Vol-pct plate examined	Inclusion size range, mm	Inclusion nitrogen content, pct[5]
15	Control..................	None	39	-	None	20.8	-	-
35[1]	.....do..................	None	33	-	None	([4])	-	-
25	Air-contaminated Mg......	9,200	4,170	45	27	.37	0.1-1.3	12
36[1]	.....do..................	11,900	2,870	24	5.0	.46	.1- .4	5
78	.....do..................	5,700	2,530	44	2.2	2.0	.1-1.0	14
85	.....do..................	5,600	890	16	5.1	2.4	.2-1.0	None.
26	Discontinuous diffuse air leak, during reduction..	3,400	1,990	59	None	13.2	-	-
51	.....do..................	5,900	1,380	23	None	6.1	-	-
68	.....do..................	12,300	3,630	30	None	12.2	-	-
29	Continuous diffuse air leak, during reduction..	7,000	1,700	24	None	21.4	-	-
52	.....do..................	9,800	1,950	20	None	7.7	-	-
69	.....do..................	14,700	3,880	26	None	7.0	-	-
34	Continuous localized air leak, during reduction..	2,800	745	27	None	23.3	-	-
55	.....do..................	5,600	1,590	28	None	9.4	-	-
70	.....do..................	8,300	3,760	45	.38	.98	.1- .2	2
82	.....do..................	9,600	5,110	53	7.0	2.5	.1-1.0	5-9
39	Continuous diffuse air leak, during distillation...........	10,600	7,830	74	190	.56	.1-2.0	6-8
50	.....do..................	12,200	4,210	35	30	1.2	.1-1.5	2-14
39B[2]	.....do..................	-	-	-	9.4	2.0	.1- .8	10
75	.....do..................	5,400	4,700	87	12	2.0	.2-1.7	3-8
42	Continuous localized air leak, during distillation...........	4,900	3,520	72	6.1	1.7	.1-3.0	8
59	.....do..................	5,100	5,790	100	64	.95	.1-18	9
42B[2]	.....do..................	-	-	-	None	10.4	-	-
59B[2]	.....do..................	-	-	-	.97	1.9	.3-1.0	8-13
74	.....do..................	2,600	2,700	100	6.5	1.3	.2-1.5	3-9
57	Continuous air leak during helium sweep.....	6,100	2,960	49	.12	4.6	.5-1.5	2-5
58	.....do..................	5,800	2,040	35	None	12.7	-	-
71	.....do..................	4,900	1,880	38	None	5.4	-	-
84	.....do..................	10,400	7,000	67	31	1.5	.1-4.0	2-9
84B[2]	.....do..................	-	-	-	6.8	1.9	.2- .4	None.

[1] Double melted ingot--all others single melted.

[2] Remelt of ingot of preceding number.

[3] Calculated from weight of nitrogen added and weight of sponge produced.

[4] No data,

[5] Analysis by electron microprobe.

Defect-Particle Seeding

The production of nitrided titanium sponge pieces and burned fragments and their seeding into the reduction retort or the distillation retort during sponge production have been described in the experimental section of the report. Location of high-nitrogen or oxy-nitride defects in titanium sponge was the most difficult operation in the study. Hydriding and grinding, chlorination, infrared reflectivity, and visual observation described before were unsuccessful.

Seeding of artificial defects was done in order to observe what a high-nitrogen defect may look like in a sponge mass. Two important findings were made when either nitrided or air-burned sponge pieces of about 1 gram in weight were seeded during the reduction cycle. First, the characteristic yellow color of the nitrided piece or the multicolor of the burned fragment disappeared, and the fragment took on nearly the same color and texture as the host sponge. Second, the fragments acted as nuclei for sponge growth. They were, in many cases, found completely clad with newly formed sponge. (See figures 11 and 12.)

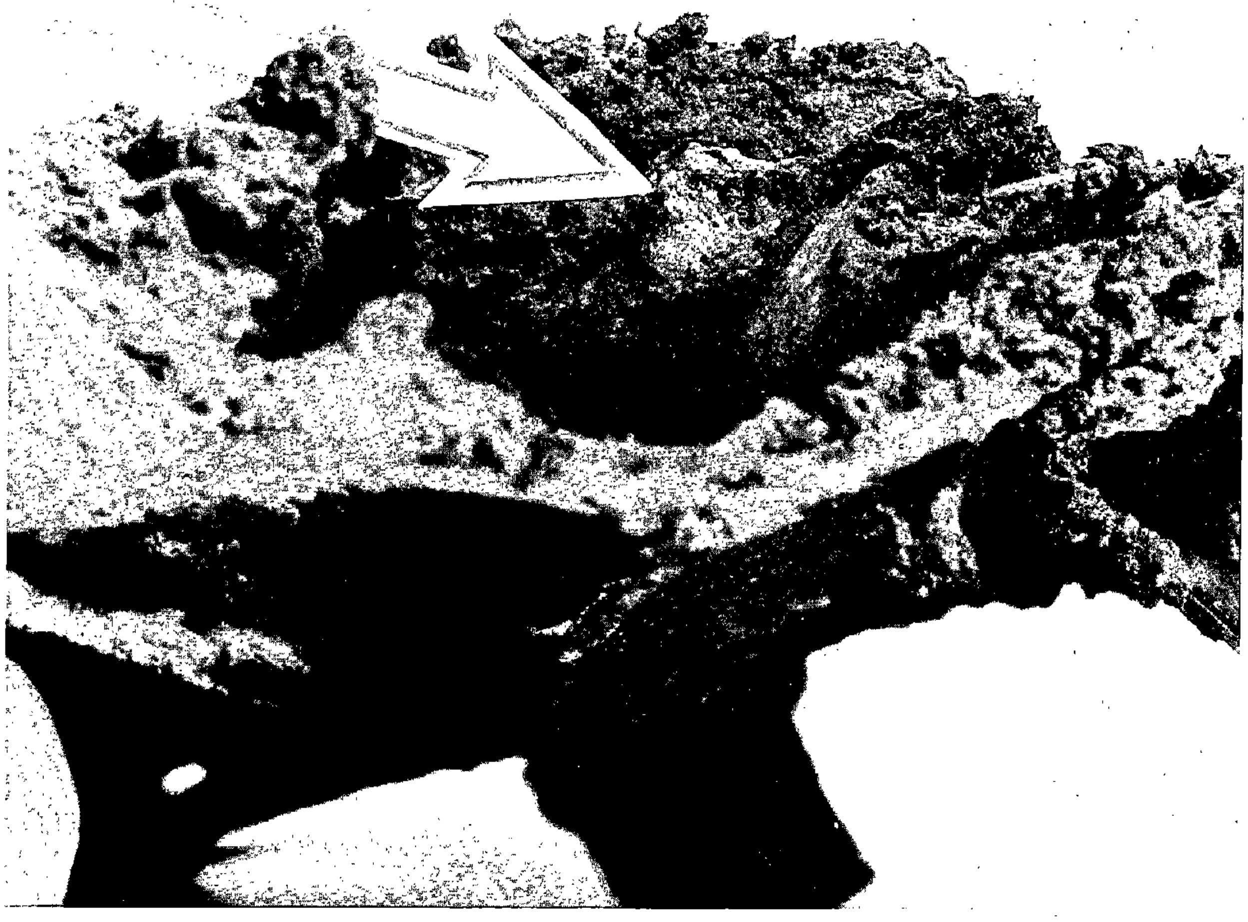


FIGURE 11. - Nitrided sponge piece found after seeding in reactor during $TiCl_4$ reduction.

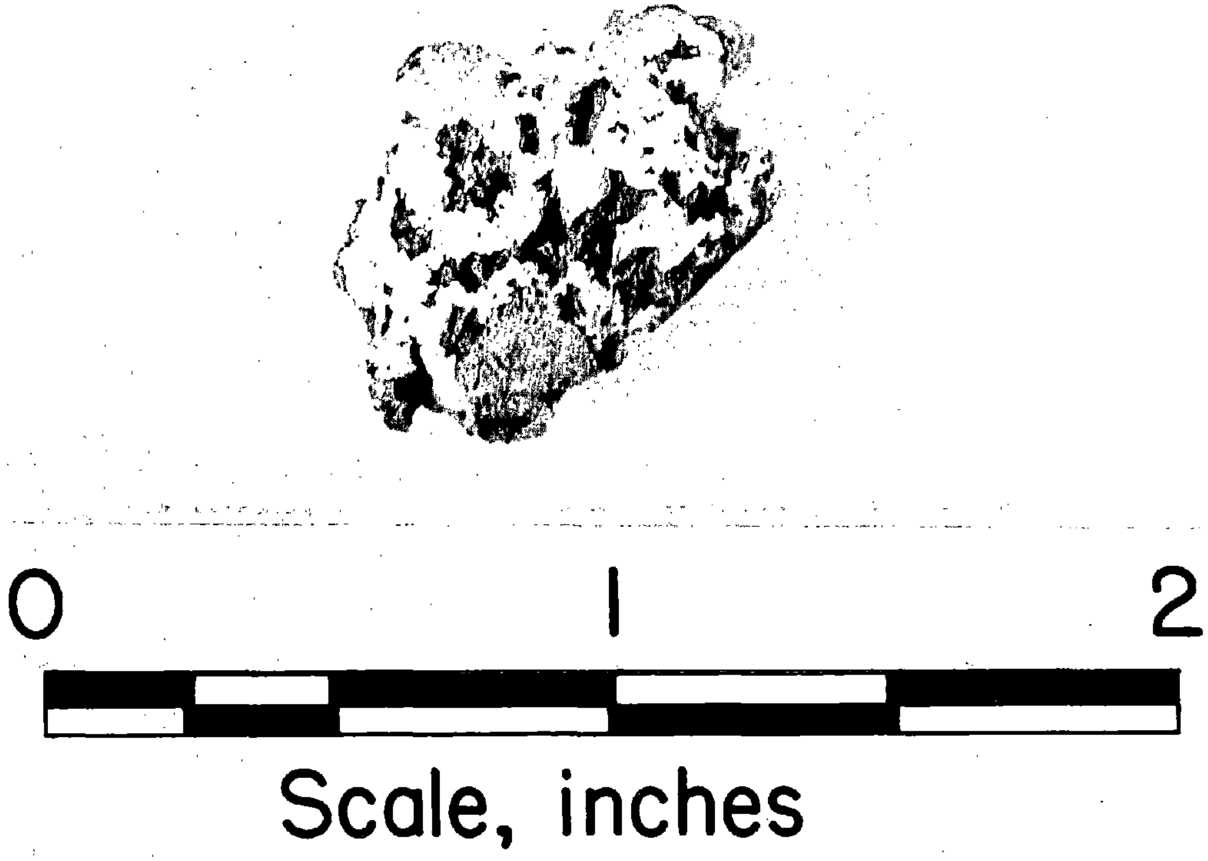


FIGURE 12. - Nitrided sponge piece seeded into reactor showing cladding by newly formed sponge.

Both nitrided and air-burned fragments also lost their characteristic color when seeded into the sponge in the distillation cycle. Thus it may be concluded that visual inspection of titanium sponge for defect pieces based on coloration is unreliable. Only pieces that react with air after opening the retort are likely to exhibit color.

Role of Air-Contaminated Magnesium

Thermodynamics

It has often been suggested that the magnesium nitride contained in the dross of air-contaminated magnesium may react with $TiCl_4$ or with titanium to produce particles of high-nitrogen sponge which, in turn, may cause defects in ingots. Nitride-containing dross has been observed in sponge removed from commerical retorts, and the adjacent sponge has been found to be abnormally high in nitrogen. However, formation of ingot inclusions from this source has never been demonstrated.

Thermodynamically, the reaction between magnesium nitride and either Ti or $TiCl_4$ is favorable (5):

$$Mg_3N_2 + 2\ Ti \rightarrow 2\ TiN + 3\ Mg \quad \Delta G^\circ_{800^\circ\ C} = -55{,}000\ cal$$

$$Mg_3N_2 + 2\ TiCl_4 \rightarrow 2\ TiN + 3\ MgCl_2 + Cl_2 \quad \Delta G^\circ_{800^\circ\ C} = -98{,}000\ cal.$$

Laboratory Experiments

Small-scale laboratory tests were conducted to investigates the feasibility of the reaction between MG_3N_2 and Ti or $TiCl_4$ to form titanium nitride. Stoichiometric mixtures of Ti and Mg_3N_2 powders were pelletized and heated in argon for 1 hour at 750°, 900°, and 1,000° C. At 900° C, a trace of ε-Ti_2N was detected in the product by X-ray Diffraction. At 1,000° C, traces of both ε-Ti_2N and δ-TiN were detected.

Magnesium nitride particles were also reacted in a stream of gaseous $TiCl_4$ for 1 hour at 750°, 900°, and 1,000° C. A trace of δ-TiN was found in the product of the 900° C experiment only. Other experiments were also conducted in which Mg_3N_2 was reacted with $TiCl_4$ in the presence of magnesium, and in which Mg_3N_2 was reacted with Ti and $TiCl_4$ simultaneously. Titanium subchlorides, $TiCl_2$ and $TiCl_3$, were found in the product, but no titanium nitrides. The three positive results indicate that nitrogen is transferred from magnesium nitride to the titanium.

Magnesium Nitride Seeding of Sponge

The laboratory experiments previously described were followed by further experiments in which 1/2- to 1-gram pieces of dense pure Mg_3N_2 were seeded into the 12-inch Kroll reactor during the reduction of $TiCl_4$ by molten magnesium. All of the pieces of Mg_3N_2 were located in the resulting sponge cake because of their yellow color, white hydrolysis product, and ammonia odor. A small amount of brown residue was found adjacent to each piece of Mg_3N_2. This residue was found by X-ray diffraction to be ε-Ti_2N and δ-TiN.

To increase the surface area to promote reaction, a second test was conducted in which 11 1-gram charges minus 60-mesh Mg_3N_2 powder in sealed magnesium capsules were seeded into the reactor during the reduction operation. Four capsules were added to the molten magnesium pool prior to the introduction of $TiCl_4$. This was done to simulate a dross of Mg_3N_2 on the surface of the molten magnesium.

More reaction product was found at the Mg_3N_2 powder sites, and X-ray analyses of the residual material showed it to contain both δ-TiN and ε-Ti_2N. Figure 13 shows the site of a pocket of Mg_3N_2 powder which has reacted to form Ti_2N and TiN. The product is the dark material near the hole in the sponge.

Titanium nitride was found at the bottom of the sponge cake also. The source of this nitride may be the Mg_3N_2 that was seeded onto the molten magnesium surface.

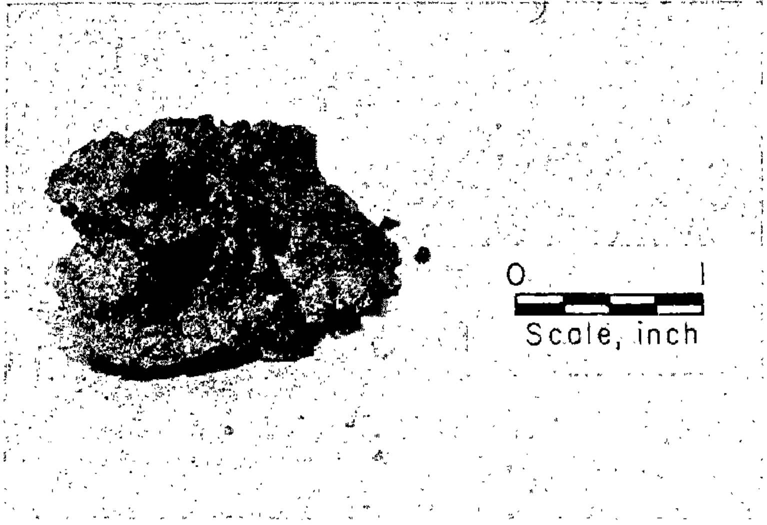


FIGURE 13. - Site of pocket of Mg_3N_2 powder in sponge. Dark material is titanium nitride product.

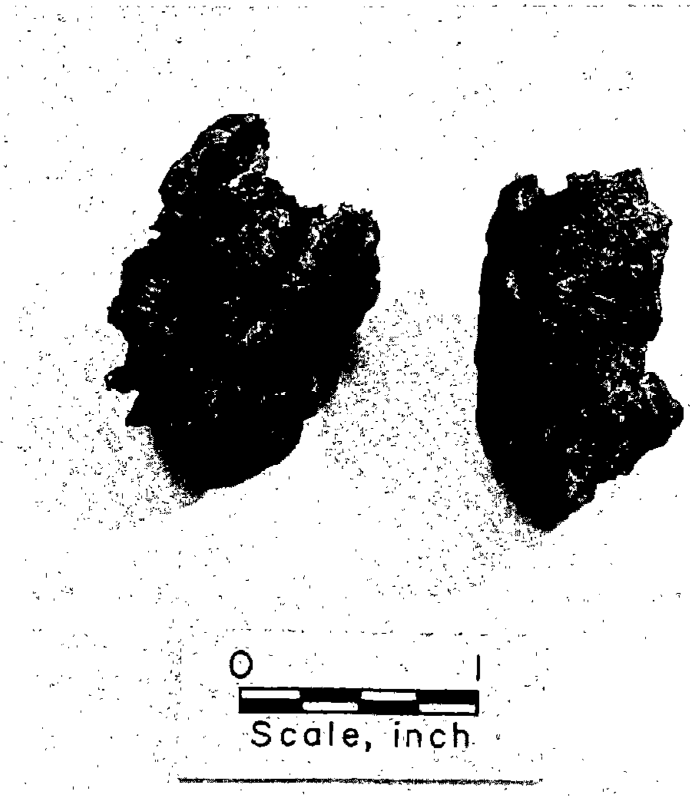


FIGURE 14. - Typical pocket of friable high-nitrogen sponge located in sponge cake.

Sponge Production From Contaminated Magnesium

The laboratory experiments, together with the Mg_3N_2 seeding experiments, definitely prove that the nitrogen contained in Mg_3N_2 is chemically transferred to the titanium to produce both ϵ-Ti_2N and δ-TiN. They do not, however, prove that Mg_3N_2 is a source of nitride inclusions in titanium ingots.

To investigate Mg_3N_2 as a source of alpha-stabilized nitride inclusions, a series of sponge production runs was made in which nitrogen-contaminated or air-contaminated magnesium was employed as a reductant. Reaction of both nitrogen and air with molten magnesium at 800° C produced a dross that floated on the surface. Nitrogen was entirely reacted to Mg_3N_2 and the oxygen to MgO. In each case, the nitrogen and oxygen content of the dross-free metal was not significantly different from that of the pure magnesium pig. These observations are in good agreement with the reported low solubility of MgO and Mg_3N_2 in magnesium (1). When as little as 7 percent of the normal magnesium charge had reacted with $TiCl_4$, the $MgCl_2$ formed wetted much of the dross and caused it to sink in the molten magnesium.

Reaction of nitrogen-contaminated magnesium with $TiCl_4$ resulted in sponge containing much δ-TiN in the form of submicrometer-size golden-brown powder. Some of the powder was loose in the bottom region of the sponge and crucible and some was in the form of pockets and friable lumps on and near the bottom of the sponge cake. Figure 14 illustrates a typical pocket of friable high-nitrogen sponge located near the bottom of the cake.

Reaction of air-contaminated magnesium with $TiCl_4$ produced a sponge contaminated with pockets, friable lumps, and unattached powder consisting of both TiN and MgO.

Plates made from both single-melt and double-melt ingots from the air-contaminated magnesium-run sponge contained small alpha-stabilized inclusions. These inclusions ranged in size from less than 0.1 millimeter to 1.3 millimeters and in nitrogen content from 5 to 12 percent. Frequency of inclusions from single-melt ingot plate was 27 defects per cubic centimeter. The frequency of inclusions from the double-melt ingot plate was five defects per cubic centimeter.

Data are shown in table 3, runs 25, 36, 78, and 85, and a typical defect is illustrated in figure 15.

The nitrogen balance and distribution for a separate lot of sponge made from air-contaminated magnesium are given in table 4. The loose powder contains 117,000 ppm nitrogen, but only 26 percent of the nitrogen is accounted for. Much of the nitrogen and oxygen reacted with condensed magnesium vapor on the retort walls and was isolated from the sponge.

TABLE 4. - Nitrogen balance of sponge from air-contaminated magnesium

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Side, porous	961	165	0.16
Side, dense	748	850	.64
Heart	1,247	56	.07
Top	720	209	.15
Top ring	642	658	.42
Top rim	198	1,260	.25
Bottom	710	2,490	1.77
Bottom rim	448	1,140	.51
Loose powder	42	17,000	4.91
Loose sponge	92	21,300	1.96
Hard sponge and powder	42	91,500	3.84
Total recovered	5,850	-	14.68
Originally present	5,876	-	57.1
Percent accounted for	99.6	-	25.7

Molten Magnesium Filtration Tests

Four separate charges of magnesium were melted and subjected to controlled air contamination in the apparatus shown in figure 10. Two of these charges were filtered through a steel wool filter pad into 11-inch-diameter

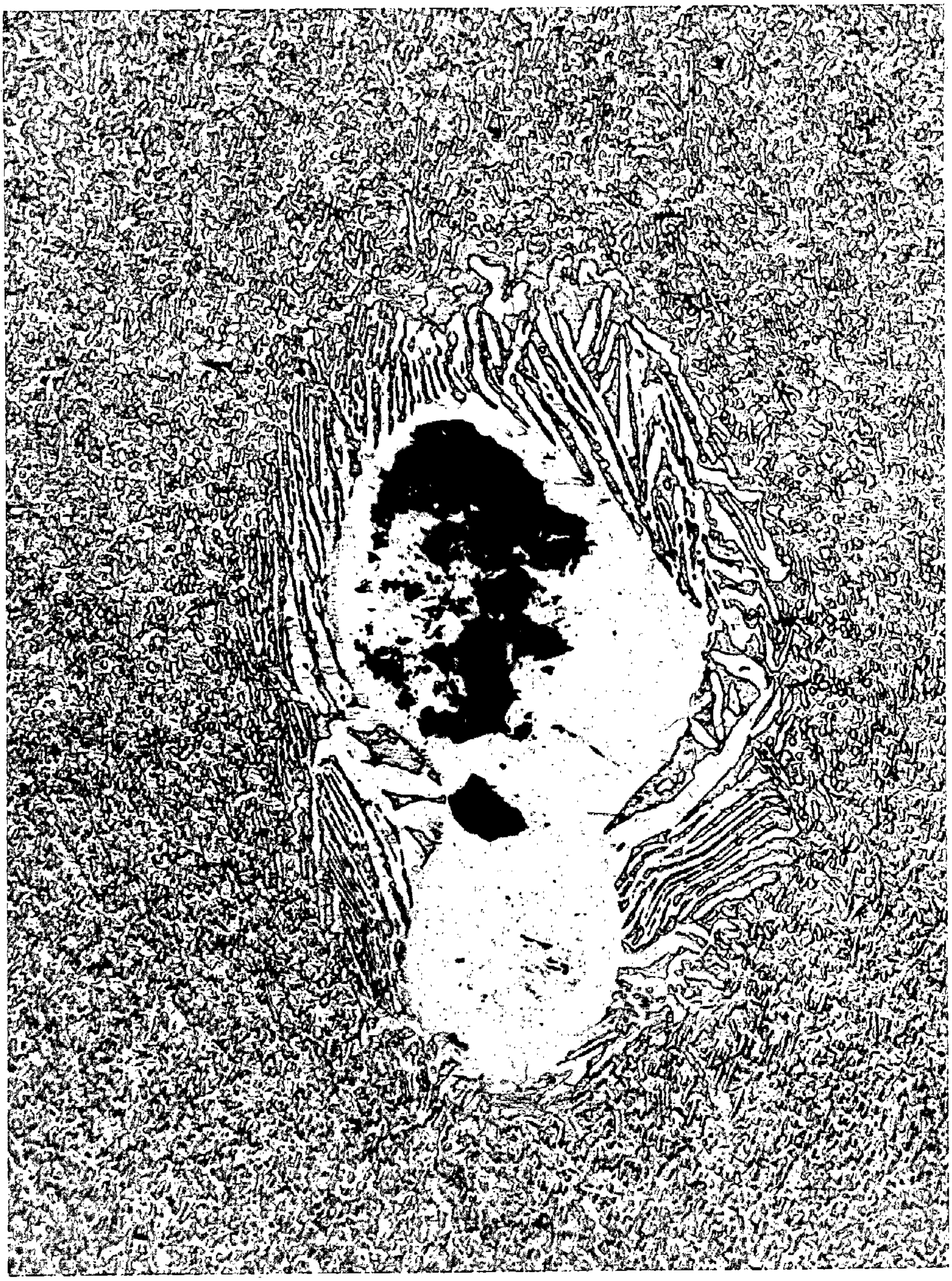


FIGURE 15. - Typical nitride inclusion found in plate made from sponge reduced by air-contaminated magnesium, X 50.

reduction crucibles, and the other two were allowed to flow into reduction crucibles without passing through a filter pad. Each lot, in turn, was used as a reductant to produce a batch of titanium sponge. The resulting sponge was melted into ingots and hot-worked into 1/2-inch plates for analysis and inclusion inspection.

Data for these experiments are given in table 5. It may be seen that the nitrogen content of the two plates prepared from sponge made from filtered magnesium is 102 and 191 ppm compared with 1,440 and 2,907 ppm for plates made from sponge reduced by unfiltered magnesium.

TABLE 5. - Effect of filtration of air-contaminated magnesium on the incidence of nitride inclusions in hot-rolled plate

Run No.	Sponge treatment	N_2 added as air, ppm[1]	Nitrogen in plate, ppm	Nitrogen retention, pct	Inclusions found per cubic centimeter	Vol-pct plate examined	Inclusion size range, mm	Inclusion nitrogen content, pct[2]
60	Filtered air contaminated magnesium...	10,000	102	1.0	None	25.1	-	-
77	.....do..................	10,900	191	1.8	None	18.8	-	-
63	Unfiltered-air contaminated............	8,990	1,440	16	0.53	2.0	0.2-9.0	>10
72	.....do..................	11,000	2,907	26	.91	1.9	.1- .5	1.7-9.4

[1] Calculated from weight N_2 added and weight-percent sponge produced

[2] Analysis by electron microprobe.

The important result is the fact that nitride inclusions were found in both plates prepared from sponge from unfiltered magnesium and none were found in the destructive testing of 25 and 19 percent of the plates made from sponge reduced by filtered magnesium.

The low percentage of nitrogen retention shown for the unfiltered-magnesium experiment is due partly to the fact that much dross adhered to the walls of the melting chamber when the molten magnesium was allowed to flow into the reduction crucible.

Simulated Air Leaks During Sponge Production

Three different types of simulated air leaks during the reduction cycle, two types during the distillation cycle, and one during a helium sweep cycle were employed to study the nitrogen distribution in the resulting sponge and to determine if the resulting nitrides were capable of surviving arc-melting to produce inclusions in ingots. Two or more levels of air contamination were studied in each test. As explained in the experimental section of this report, the nitrogen levels were made deliberately high to increase the probability of finding inclusions should they result from the treatment. In each air-leak study, one lot of sponge was consumed for analytical samples and the other lots were arc-melted into ingots, which were, in turn, forged and rolled into plate. Data for these experiments are presented in table 3.

Discontinuous Diffuse Leak During Reduction

In this test, five separate bursts of air were added at even time intervals during the reduction cycle as explained in the experimental section. For the nitrogen distribution study, 18.2 grams of nitrogen as air were added during the run. Nitrogen distribution is shown in table 6. It will be noticed that only 40 percent of the nitrogen is accounted for and that the highest nitrogen content is only 0.65 percent. Much of the air was probably consumed by the sponge formed high on the retort walls from condensed magnesium. A trace of both TiN and Ti_2N was identified in the sponge by X-ray diffraction.

TABLE 6. - Nitrogen balance of sponge from discontinuous diffuse leak during reduction

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Side above bottom ring.....	1,715	1,220	2.09
Bottom surface............	126	861	.11
Bottom center.............	146	1,023	.15
Bottom ring...............	638	312	.20
Lower heart...............	223	650	.15
Upper heart...............	444	2.85	.13
Top.......................	720	2,290	1.65
Top ring..................	883	1,740	1.54
Unassigned................	212	6,550	1.39
Total recovered...........	5,107	-	7.41
Originally present.........	5,500	-	18.2
Percent accounted for......	92.9	-	40.7

For the inclusion study, three levels of nitrogen as air were introduced, 18, 36, and 64 grams, representing 3,400, 5,900, and 12,300 ppm, respectively, of nitrogen based on the weight of the sponge produced. As shown in table 3, runs 26, 51, and 68, no nitride inclusions were located during the destructive testing of 6.1 to 13.2 volume-percent of the plates.

Continuous Diffuse Leak During Reduction

In these tests, air was continuously metered into the retort during the entire reduction cycle. For the nitrogen distribution study shown in table 7, 44.5 grams of nitrogen as air was introduced. Only 30 percent of the nitrogen is accounted for, and the highest nitrogen concentration is 0.76 percent. Neither TiN nor Ti_2N were detected in the sponge by X-ray diffraction.

For the inclusion study, three levels of nitrogen as air were employed, 40, 60, and 80 grams, representing 7,000, 9,800, and 14,700 ppm, respectively, of nitrogen based on the weight of the sponge produced. Data are given in table 3, runs 29, 52, and 69. It may be seen that no nitride inclusions were found in the destructive examination of 7 to 21.4 volume-percent of the plates.

TABLE 7. - Nitrogen balance of sponge from continuous diffuse leak during reduction

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Side, porous...............	514	5,110	2.62
Bottom....................	797	2,060	1.64
Side, dense................	1,517	1,760	2.67
Top, rim..................	551	3,400	1.87
Heart.....................	1,012	1,320	1.34
Sidewall..................	378	7,600	2.87
Unassigned................	53	6,400	.34
Sidewall, brittle..........	12	6,500	.08
Total recovered............	4,834	-	13.43
Originally present.........	5,682	-	44.5
Percent accounted for......	85.1	-	30.2

Continuous Localized Leak During Reduction

Introduction of air through a titanium tube into the heart region of the sponge during its formation has been explained in the experimental section. To study the nitrogen distributuion in the sponge cake, 15 grams of nitrogen as air was admitted. From the data given in table 8, it may be seen that essentially all of the nitrogen was retained by the sponge. Near the region of the air leak, the nitrogen content is shown to be 37,600 to 98,100 ppm whereas that of the heart region is only 48 ppm. A trace of TiN and a larger amount of Ti_2N were found by X-ray diffraction.

TABLE 8. - Nitrogen balance of sponge from continuous localized leak during reduction

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Top rim.........................	849	2,040	1.73
Top.............................	452	192	.09
Top rim, near leak...............	96	1,190	.11
Heart...........................	621	48	.03
Side, porous.....................	510	45	.02
Side, dense......................	944	2,910	2.75
Bottom ring......................	1,053	8,230	8.67
Bottom..........................	240	3,240	.78
Unassigned......................	86	5,600	.48
Side, near leak..................	110	4,550	.50
Black powder in bottom ring......	2	98,100	.20
Brittle zone, near leak..........	15	36,700	.55
Brittle dark sponge near leak....	4	68,100	.27
Total recovered..................	4,982	-	16.18
Originally present...............	5,227	-	15.1
Percent accounted for...........	95.3	-	107

Three different levels of nitrogen as air were employed in the four experiments of the inclusion study, 15, 30, 53, and 50 grams representing 2,800, 5,600, 8,300, and 9,600 ppm, respectively, based on the weight of sponge produced. Data in table 3, runs 34, 55, 70, and 82 show no inclusions located at the 2,800- and 5,600-ppm levels, in the destructive inspection of 23.3 and 9.4 volume-percent of the plates. At the 8,300-ppm level a very low incidence in inclusions, 0.38 inclusion per cubic centimeter was observed. The inclusions range in size from 0.1 to 0.2 millimeter and have a nitrogen content of 2 percent. At the 9,600-ppm level the incidence is seven inclusions per cubic centimeter. They range from 0.1 to 1.0 millimeter in size and 5 to 9 percent nitrogen.

Continuous Diffuse Leak During Distillation

A total of 58 grams of nitrogen as air was introduced in the nitrogen distribution study shown in table 9. Only 53 percent of the nitrogen was retained in the sponge. Most of the nitrogen appeared on or near the top surface where the air was introduced. Considerable TiN and Ti_2N were detected by X-ray diffraction in this region.

TABLE 9. - Nitrogen balance of sponge from continuous diffuse leak during distillation

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Top surface	393	25,700	10.10
Upper heart	367	2,600	.95
Lower heart	917	1,160	1.06
Bottom ring	1,310	1,140	1.49
Bottom	340	1,330	.45
Sidewall	478	7,250	3.47
Sides	1,410	2,610	3.68
Unassigned	334	23,300	7.78
Top surface, brittle, colored	14	58,500	.82
Subsurface layer	6	108,000	.65
Surface, golden	4	117,000	.47
Total recovered	5,573	-	30.92
Originally present	5,591	-	58
Percent accounted for	99.7	-	53.3

Two levels of nitrogen as air were employed in the inclusion study of this type of air leak, 58 and 30 grams of nitrogen representing 10,600, 12,200, and 5,400 ppm in the three runs based on the weight of sponge produced. Table 3, runs 39, 50, 39B, and 75, shows that inclusions were found in the hot-rolled plate from all three lots of sponge and even in the plate from a remelted plate. The inclusion incidence of the plate from run 39, 190 inclusions per cubic centimeter, dropped to 9.4 inclusions per cubic centimeter when the plate was remelted and hot-rolled into plate again. A typical inclusion is shown in figure 16.

FIGURE 16. - Typical nitride inclusion found in plate made from sponge contaminated by diffuse air leak during distillation, X 50.

Continuous Localized Leak During Distillation

For the study of nitrogen distribution, 29 grams of nitrogen as air was introduced into the heart region of the sponge through a titanium tube as described in the experimental section. Data in table 10 show that 91 percent of the nitrogen was retained by the sponge. Most of the nitrogen appears in the heart region where the leak was concentrated. Considerable TiN and Ti_2N were detected by X-ray diffraction.

TABLE 10. - Nitrogen balance of sponge from continuous localized leak during distillation

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Top	617	661	0.41
Upper heart	533	1,940	1.03
Lower heart	260	9,570	2.49
Upper side	720	6,720	4.85
Lower side	1,542	7,430	11.46
Bottom	879	6,380	5.61
Sidewall	490	1,344	.66
Total recovered	5,042	-	26.5
Originally present	5,216	-	29
Percent accounted for	96.7	-	91.4

Data on the inclusion study are presented in table 3, runs 42, 59, 42B, 59B, and 74. Two different nitrogen levels were examined, 29 and 15 grams, representing 4,900, 5,100, and 2,600 ppm based on the weight of the sponge produced in the three runs.

Inclusions were found in the hot-rolled plates from all three runs and also in the remelted plate 59B. The inclusion incidence was lowered in plate 42 from 6.1 inclusions per cubic centimeter to zero (none observed in destructive inspection of 10.4 volume-percent of plate) on remelting of plate. The inclusion incidence of plate 59 was lowered from 64 to 0.97 inclusions per cubic centimeter by remelting. A typical inclusion from this series of air leaks is shown in figure 17.

Continuous Diffuse Leak During Helium Sweep

A total of 29 grams of nitrogen as air was introduced into the helium stream during the simulated helium sweep of run 48 for the nitrogen distribution study shown in table 11. Only 35 percent of the nitrogen was accounted for and the highest nitrogen concentration was 4.15 percent on the top surface of the sponge cake. Both Ti_2N and TiN were detected in the sponge by X-ray diffraction.

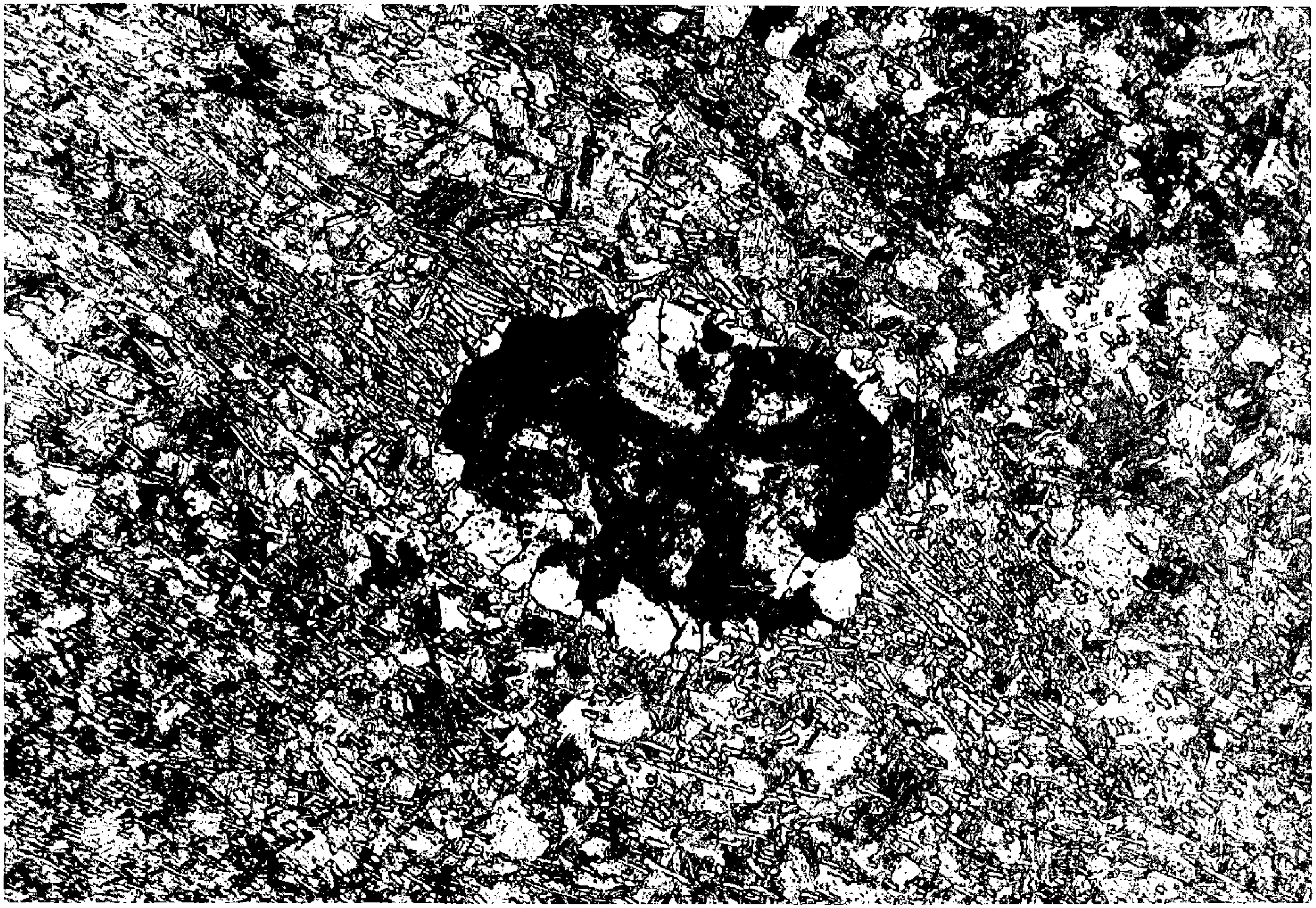


FIGURE 17. - Typical nitride inclusion found in plate made from sponge contaminated by localized air leak during distillation, X 50.

TABLE 11. - Nitrogen balance of sponge from continuous air leak during helium sweep

Region	Weight of sponge, grams	Nitrogen, ppm	Weight of nitrogen, grams
Top rim....................	183	14,300	2.62
Top surface................	87	41,500	3.61
Bottom plate...............	135	930	.012
Heart......................	1,050	14	.015
Bottom.....................	1,584	67	.106
Sides......................	1,119	2,340	2.61
Top........................	964	1,300	1.25
Total recovered............	5,122	-	10.22
Originally present.........	5,909	-	29.3
Percent accounted for......	86.7	-	34.9

Two levels of nitrogen, 30 and 60 grams, representing 6,100, 5,800, 4,900, and 10,400 ppm in the four runs based on sponge weight were employed in sponge runs for plate evaluation. Data are shown in table 3, runs 57, 58, 71, and 84. One of the three low-contamination level runs resulted in an inclusion incidence of 0.12 inclusion per cubic centimeter. The inclusions ranged in size from 0.5 to 1.5 millimeters and in nitrogen content from 2 to 5 percent.

At the 10,000-ppm nitrogen level, a very high inclusion incidence was found, 31 inclusions per cubic centimeter. As in the leak test during distillation, these results show how sensitive sponge is to nitridation during helium sweep.

NITRIDE DEFECT SURVIVAL--MISCELLANEOUS EXPERIMENTS AND GENERAL DISCUSSION

Physical Condition of High-Nitrogen Material in Sponge

In none of the air-contamination experiments were dense hard particles of titanium nitride found in the sponge. Rather, the nitride and oxide were in the physical form of friable pieces, loose powder, and pockets of powder. This observation came somewhat as a surprice since, because of the dense-particle seeding work of Wood (9), we had expected that high-density nitride particles were probably the source of real inclusions in titanium ingots. Indeed, it was for such hard, dense particles that we had been searching.

In the sponge made from nitrogen contaminated and air-contaminated magnesium most of the high-nitrogen material was found as a loose powder in the bottom of the crucible, a layer of loose powder on the bottom of the sponge cake and pockets of powder and relatively low-density friable pieces extending an inch or two up into the sponge cake from the bottom surface. Figure 14 shows pockets of high-nitrogen powder and figure 18 illustrates the location of high-nitrogen powder.

FIGURE 18. - High-nitrogen powder found on and near bottom of sponge cake reduced by nitrogen-contaminated magnesium.

Low-density, friable material containing high-nitrogen was also found in the sponge made during simulated air leaks. The material was dispersed throughout the sponge cake in the product of diffuse air leak experiments but concentrated near the point where air was introduced in the localized air leak experiments.

Sinterability of Titanium Nitride Found in Contaminated Sponge

If defect sponge containing a high-nitrogen content consisted of very hard, high-density particles, it would not be difficult to visualize survival during arc melting. Delta TiN, having a density of 5.44 g/cm^3 and a melting point of 2,950° C, could be expected to sink rapidly in the molten titanium pool and deposit on the solidification interface before it had a chance to go into solution.

Since the high-nitrogen sponge observed in the experiments reported here were not high-density particles but rather fine powder or relatively soft friable pieces, it is difficult to understand how they could survive arc melting. This is expecially true since the dispersion of titanium nitride powder in sponge electrodes is a technique used in industry to increase the soluble nitrogen content of titanium metal.

Several miscellaneous experiments were conducted in an attempt to gain a better understanding of the mechanism of survival of the undensified form of TiN and Ti_2N observed in the sponge.

Several electrode stubs were cut in half, micropolished, and examined for nitride defect areas. The ingots associated with these stubs contained high-nitrogen inclusions. In several cases, high-nitrogen particles were found within 1/2 inch of the tip of the electrode stub. Scratch tests showed these particles to be much harder than the matrix metal, and electron microprobe examination showed them to contain substantial nitrogen

Further experiments were conducted to determine the sinterability of the TiN produced in sponge from nitrogen addition and from air addition. The TiN found in titanium sponge made from nitrogen-contaminated magnesium was a golden-brown powder containing 17.5 weight-percent nitrogen and essentially of submicrometer particle size. This powder was sintered at several temperatures and times after cold pressing at different pressures. A commercial brand TiN powder was employed as a comparison on all of these sintering tests. The sinterability of the submicrometer TiN powder was highly superior to the commercial product. Densities as high as 70 percent of theoretical were attained in 10 minutes when pellets cold-pressed at 20,000 psi were sintered

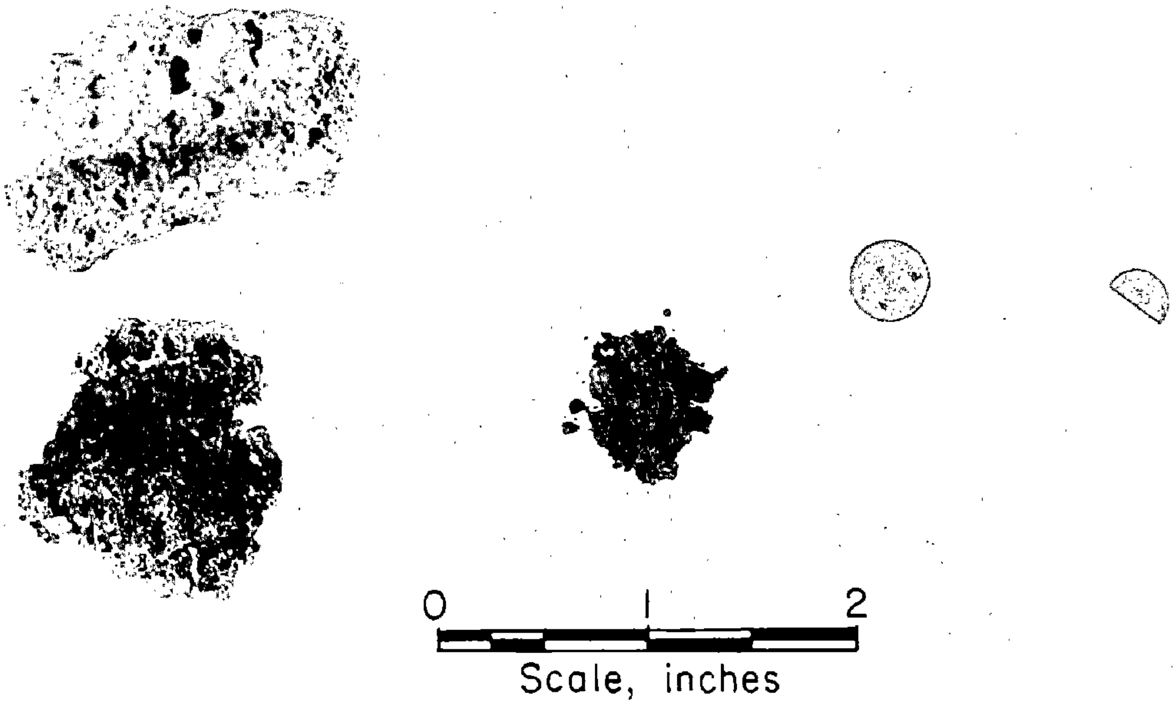


FIGURE 19. - Titanium nitride powder in sponge, after cold-pressing and after sintering.

at only 1,300° C. Figure 19 shows a pocket of TiN powder in one piece of sponge, TiN powder adhering to the surface of another piece of sponge, the powder after removal and after cold pressing, and the resulting sintered pellet.

Since pressures and temperatures attained in sponge electrode pressing and melting exceed these values, it is conceivable that high-nitrogen powder could sinter to reasonable high density in the electrode during the arc-melting operation.

High-nitrogen powder and friable pieces found in other air-leak sponge runs proved to sinter well also at relatively low pressures and temperatures. The latter material contained considerably more titanium and oxygen than the pure TiN described before, and the pellets were undoubtedly TiN-Ti cermets containing some Ti_2N and some TiO_2.

Behavior of Sintered Titanium Nitride Pellets in Molten Titanium

Half-gram pellets of sintered TiN described in the previous section were placed in drilled holes in 60-gram cubical blocks of pure titanium, plugged with a titanium cap; and button melted to observe their behavior. When the titanium became molten, the TiN pellet appeared to rise to the surface of the liquid button. The pellet moved about in an erratic manner resembling the behavior of a pad of butter on a hot frying pan. Obviously this movement is the result of gas evolution by the decomposition reaction

$$TiN \rightarrow Ti + 1/2\ N_2.$$

In a typical test, after about 10 seconds the pellet was found, by examination, to have been partially infiltrated with titanium and to have begun exfoliating. In less than 60 seconds, the pellet was reduced to tiny millimeter-size fragments. Figure 20 shows the pellet, the titanium cube, and a dissected button showing a pellet after about 10 seconds; pellet fragments

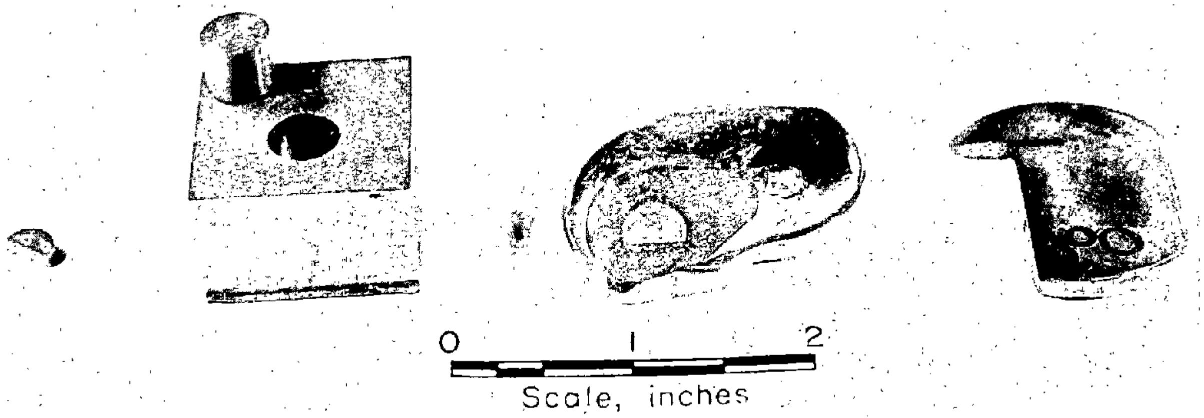


FIGURE 20. - Titanium-nitride-sintered pellet, titanium cube and cap, button after melting and machining showing pellet after 10 seconds, and button after machining showing pellet fragments after 60 seconds (encircled).

FIGURE 21. - Titanium nitride pellet after 10 seconds in molten titanium, showing infiltration.

FIGURE 22. - Photomicrograph of TiN fragment after 60 seconds in molten titanium, X 50.

after about 60 seconds are shown at the far right. Figure 21 shows a pellet infilitrated by molten titanium after about 10 seconds. Figure 22 is a photomicrograph (magnified 50 times) of one of the pellet fragments found in a titanium button. Notice the alpha-stabilized pattern around the periphery of the fragment.

Measurement of the diameter decrease of pellets after subjecting them to molten titanium indicated a solution rate of about 2×10^{-3} g/cm^2/sec, which compares closely with the vaporization rate of TiN at 2,000° C (3). It appears that the solution mechanism is vaporization enhanced by titanium infiltration and subsequent exfoliation. Loose TiN powder placed in apertures of titanium blocks dissolved almost immediately when the titanium became molten.

Seeding Sponge Electrodes With Titanium Nitride Powder

Failure of the vacuum pump near the end of the distillation cycle of a titanium sponge run resulted in a batch of sponge that was realistically air contaminated. Just below the top surface of the sponge cake was a yellow powder layer, which was collected and given the sample designation DFTS-300. Analysis showed the material to contain 15.06 percent nitrogen and 1.9 percent oxygen. The particle size ranged from less than 1 micrometer to about 150 micrometers, and X-ray diffraction showed the material to consist of TiN with minor amounts of Ti_2N and titanium.

This powder was employed in six electrode seeding experiments, which are described briefly as follows:

1. Ten 1-gram mounds of DFTS-300 powder were pressed into a 2,000-gram sponge electrode at 40 tons/in^2 in the following manner. One-third of the sponge was added and pressed and five 1-gram mounds placed on the new surface. Another third of the sponge was added and pressed and five 1-gram mounds placed on the new surface. Finally, the last third of the sponge was added and pressed to make the electrode. The electrode was arc-melted and the ingot hot-worked at 1,120° C into a 1/2-inch plate. An inclusion incidence of 13.8 inclusions per cubic centimeter was found. Inclusions ranged in size from 0.1 to 1.8 millimeters and contained 2.5 to 13 percent nitrogen.

2. A 2,000-gram sponge electrode was pressed and then drilled to produce 10 uniformly spaced holes 1/4 inch in diameter. One gram of DFTS-300 powder was placed in each hole with no packing and the holes plugged with titanium plugs. The electrode was melted and the ingot hot-worked into a 1/2-inch plate. This plate, too, showed inclusions with a similar incidence, 11.5 inclusions per cubic centimeter. The inclusions ranged in size from 0.2 to 6 millimeters and in nitrogen content, 5 to 11.5 percent.

3. Another 1,400-gram electrode was prepared in which 10 grams of DFTS-300 powder was uniformly dispersed between five separate layers of pressed sponge. The resulting 1/2-inch plate showed no inclusions from the destructive inspection of 30 volume percent of the plate.

4. Four holes were drilled at equal intervals along the longitudinal axis of a 2,000-gram sponge electrode. The 1/4-inch-diameter holes were drilled at a 30° angle so the powder would lie in the bottom of the hole without compression when the electrode was standing upright during arc melting. Again 1 gram of DFTS-300 powder was loosely placed in each hole and the holes plugged.

Melting was carried out until the bottom of the stub was approximately 1/2 inch below the bottom of the hole. The power was then interrupted and the electrode cooled and removed, the stub cut off, and the electrode again melted to about 1/2 inch from the bottom of the second hole. In this manner, four stubs were produced that should have contained the loose TiN powder near the melt surface.

Three of the four stubs had melted through to the hole. The stubs showed fragments of TiN greater than 1,000 micrometers in diameter. These particles, which are much larger than the largest powder particles, were found in the portion of the stub that had been molten or at the melt-sponge interface. Knoop hardness of the particles was over 900 kg/mm^2 for the adjacent solidified metal and 150 kg/mm^2 for adjacent compressed sponge.

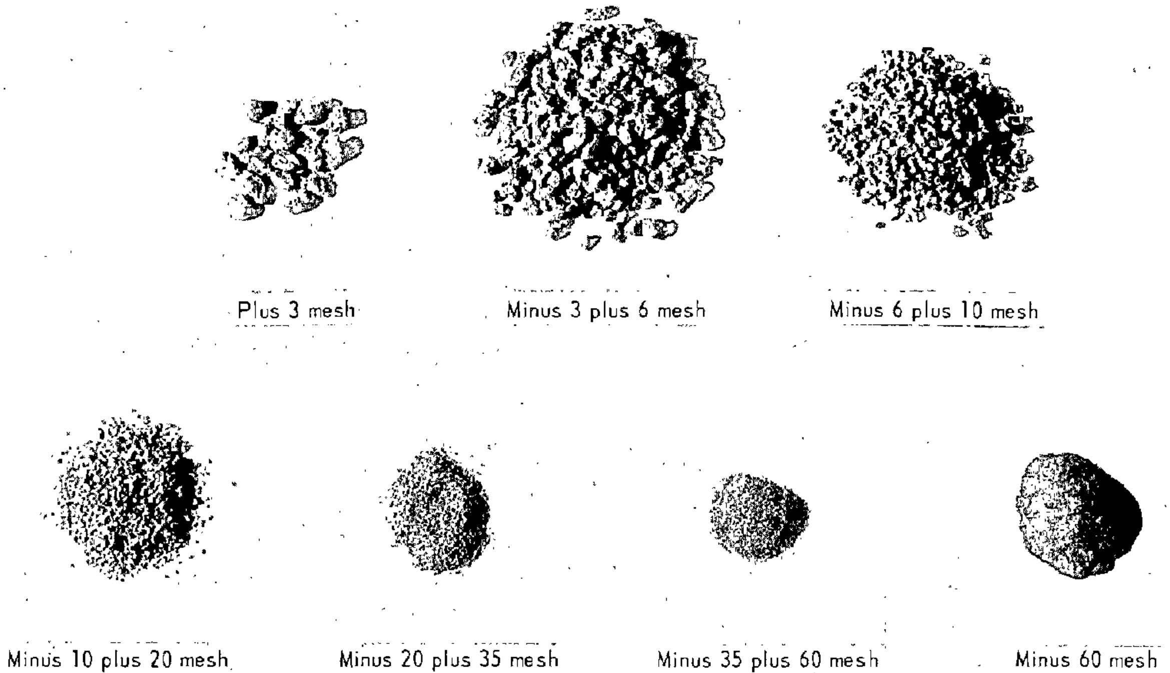
5. This test was identical to test 1 except that only a single 1-gram mound of DFTS-300 powder was seeded. The nitrogen content of the metal from the 1/2-inch slab was only one-sixth that of the slab from run 1. Inclusions were detected in one region, but they proved to be silicon carbide particles.

6. This test was identical to test 2 except only one hole was seeded with 1 gram of DFTS-300 powder. The nitrogen content was only one-eighth that of the plate from run 2, but inclusions ranging in size from 0.2 to 0.3 millimeter were found in one region. Electron microprobe analysis showed the inclusions to contain 4.8 to 6.5 percent nitrogen. These six electrode seeding experiments indicate that well-dispersed TiN powder dissolved quickly and completely during arc melting. This was also observed in the button-melting experiments.

The experiments show that TiN powder compressed at electrode pressing pressures densified sufficiently during arc melting to permit the survival of some fragments in the ingot. This was observed also in the sintering and button-melting experiments described before.

Finally, the experiments indicate that loosely packed powder concentrated in one area in the electrode is capable of agglomerating at the electrode melt surface and that this agglomerate is capable of holding together in some cases long enough to deposit on a liquid-solid interface in the melt pool and become an inclusion.

It appears rather conclusively that titanium nitride does not have to be in the physical form of a high-density particle to survive arc melting.


Plus 3 mesh

Minus 3 plus 6 mesh

Minus 6 plus 10 mesh

Minus 10 plus 20 mesh

Minus 20 plus 35 mesh

Minus 35 plus 60 mesh

Minus 60 mesh

FIGURE 23. - Relative proportions of sponge from a typical screening and sizing test.

Mechanical Attrition of Sponge

Hammermilled sponge from each air-contaminated lot was sieved into the following fractions using standard Tyler screens: Plus 3, minus 3 plus 6, minus 6 plus 10, minus 10 plus 20, minus 20 plus 35, minus 35 plus 60, and minus 60. The relative proportions of sponge in each size fraction and their physical appearance after hammermilling are shown in figure 23. Each size fraction was sampled and analyzed for both nitrogen and oxygen. Since both nitrogen and oxygen have an embrittling effect on titanium, it is not surprising that most of these interstitials are found in the finer size fractions.

The mass of sponge smaller than 20 mesh ranged from 6.6 to 12.8 percent of the total in five different runs. From 55.8 to 84.6 weight-percent of the total nitrogen added was found in this minus 20-mesh fraction and from 34.6 to 67.2 percent of the oxygen. Typical nitrogen and oxygen cumulative distribution curves are shown in figure 24. The figure shows that if the minus 20-mesh material is discarded, the sponge loss is about 12 weight-percent and the nitrogen and oxygen is reduced by 67 and 51 percent, respectively.

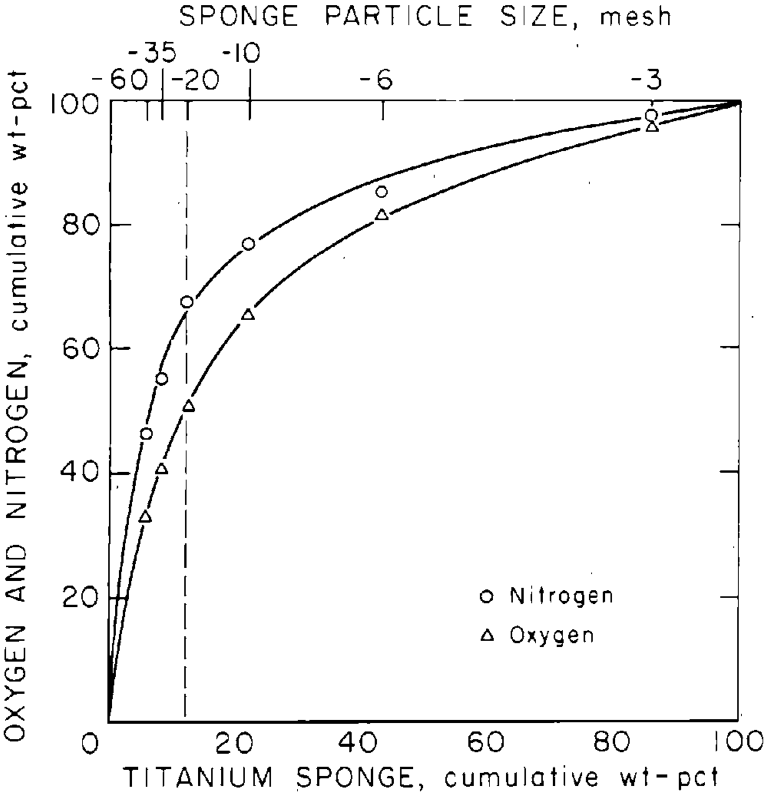


FIGURE 24. - Typical nitrogen and oxygen cumulative distribution curves for titanium sponge of cumulative size fractions.

The effect of attrition and the retention or removal of minus 20-mesh material prior to melting on the nitride inclusion index is shown in table 12. It is seen that the reduction in inclusion incidence brought about by discarding the minus 20-mesh sponge is highly significant.

It was pointed out earlier that unrealistically high levels of nitrogen had to be employed in the contamination tests in order to increase the probability of finding nitride inclusions to a practical level. It is highly likely that very small localized fragments of high-nitrogen material in sponge could be broken up and thoroughly dispersed by high-energy attrition. Ingots from this sponge should stand a much better chance of being defect-free than ingots from the same sponge without attrition.

TABEL 12. - Effect of mechanical attrition of air-contaminated sponge on the incidence of nitride inclusions in hot-rolled plate

Run No.[1]	Sponge treatment	N_2 added as air, ppm[2]	Nitrogen in plate, ppm	Nitrogen retention, pct	Inclusions found per cubic centimeter	Vol-pct plate examined	Inclusion size range, mm	Inclusion nitrogen content, pct[3]
79A	Air-oxidized Mg.......	10,600	732	6.9	0.59	2.2	0.1-0.5	[4]None.
79B	.....do...............	10,600	1,317	12	4.7	2.5	.1- .6	None.
81A	.....do...............	12,000	819	6.8	.64	2.5	.1- .5	[4]None.
81B	.....do...............	12,000	1,464	12	2.6	2.5	.1- .3	13.6
65A	Diffuse air leak during distillation..	10,200	3,156	31	4.7	1.9	.1-1	4 -15.5
65B	.....do...............	10,200	6.184	61	12.2	1.5	.1-1	4.4- 9.6
67A	.....do...............	10,600	1,715	16	4.5	1.8	.1-2.5	10
67B	.....do...............	10,600	9,100	86	146	1.9	.1-2.0	5.7-10

[1] In runs designated A, minus 20-mesh sponge was discarded before melting whereas in runs designated B, all size fractions were included in the melt.
[2] Calculated from weight of N_2 added and weight of sponge produced.
[3] Analysis by electron microprobe.
[4] Inclusion pits too deep for microprobe analysis.

SUMMARY AND CONCLUSIONS

A comprehensive experimental program has been conducted to investigate possible sources of nitride defects in the production of magnesium-reduced titanium sponge, and to determine if such defects are capable of surviving consumable-electrode-arc melting. This effort has entailed several laboratory-scale experiments and a total of 85 pilot plant sponge-production runs in a 12-inch-diameter reactor system. Sponge from over 50 of these runs was consumable-electrode-arc-melted and the resulting ingots hot-worked into plate for evaluation.

The production of alpha-stabilized nitride inclusions in hot-rolled titanium plate from air contamination of the sponge during its production has been experimentally demonstrated.

Magnesium-reduced titanium sponge, when produced by reduction by air-contaminated magnesium or when contaminated by an air leak during the reduction cycle, the vacuum distillation cycle or during an inert gas sweep cycle, shows very large variations in nitrogen content. These variations range from the extremes of 50 ppm to 120,000 ppm. The refractory nitrides, δ-TiN and ϵ-Ti_2N, have been identified in the regions of highest nitrogen in these sponge lots. The physical form of the nitrides consists of relatively porous friable fragments, pockets of fine powder or loose fine powder. In none of the sponge lots have high-density nitride particles been found. The low-density material and powder have been shown to be capable of surviving single and even double-arc melting to become inclusions in semifabricated shapes. This material may be compressed during electrode pressing and subsequently sintered by the heat of the arc to produce densified particles that survive ingot melting. Even uncompressed high-nitrogen powder, when in a sufficiently concentrated mass, is capable of consolidating during consumable-electrode melting, and the resulting impregnated mass or fragments of this mass can remain in the ingot as brittle inclusions. When high-nitrogen powder is thoroughly dispersed throughout the sponge, however, it appears to dissolve during ingot melting without leaving insoluble residue.

The highest incidence of nitride inclusions in hot-rolled plate resulted from (1) sponge reduced by air-contaminated magnesium (2) sponge subjected to an air leak during the distillation cycle, and during helium sweep, and (3) sponge subjected to highly localized leak during reduction. Inclusions were found in plates fabricated from both single- and double-melted ingots. The inclusion incidence was greatly reduced in every case by double-melting.

Diffuse air leakage during the reduction cycle was not effective in producing inclusions in the resulting hot-rolled plates. Sponge saturated with molten $MgCl_2$ appears to be less susceptible to oxidation and nitridation.

Highly colored air-burned sponge pieces and yellow nitrided sponge pieces lose their color and texture during residence in the sponge mass during either the reduction cycle or distillation cycle. During reduction, the air-burned or nitrided particle acts as a nucleus for sponge growth and is often found to be bonded in the interior of newly formed sponge. These observations indicate that color and texture may not be reliable criteria for spotting defects during sponge inspection.

The data obtained during the course of this project indicate that the incidence of nitride inclusions may be reduced by certain practices in a commercial sponge plant.

Maintaining a completely air-tight system during reduction, vacuum distillation and/or helium sweep cycles is of great importance to prevent the formation of nitrides, which may become inclusions in ingots.

Mechanical filtration of molten magnesium as it is being charged into the reduction retort to remove any nitrogen-containing dross may decrease the incidents of nitride inclusions.

High-energy impact attrition of titanium sponge in an inert atmosphere is capable of pulverizing and dispersing high-nitrogen particles. These fines may be removed to reduce the incidence of inclusions, or it is likely that the mere dispersion of the fines will promote solubilization of any contained nitride.

Tests on a commercial scale should be carried out to determine the true effectiveness of these recommendations.

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