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(54) Title: NITRIDED VALVE METALS AND PROCESSES FOR MAKING THE SAME

(57) Abstract: Nitrided valve metals are described, such as nitrided tantalum and nitrided niobium. The nitrided valve metals preferably have improved flow properties, higher Scott Densities, and/or improved pore size distribution which leads to improved physical properties of the valve metal and improved electrical properties once the valve metal is formed into a capacitor anode. Processes for preparing a nitrided valve metal are further described and involve nitriding the valve metal at a sufficient temperature and pressure during a heat treatment that is prior to the deoxidation step. Capacitor anodes and other products incorporatinng the valve metals of the present invention are further described.

NITRIDED VALVE METALS AND PROCESSES FOR MAKING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to valve metals and processes of preparing valve metals of acceptable quality for use in such applications as capacitors and the like.

There is always a desire in the industry to improve on the properties of valve metals, such as tantalum, particularly in the areas of capacitance and DC leakage achieved by valve metals when formed into capacitor anodes. The manner in which the various valve metal properties are improved upon include modifying various steps of the processes involved in making the valve metal, including purifying the valve metal.

There are general processes known to those skilled in the art for preparing valve metals. For instance, tantalum is obtained from ore and subsequently crushed into a powder. The tantalum is then separated from the crushed ore through the use of an acid solution and density separation of the acid solution containing the tantalum from the acid solution containing niobium and other impurities. The acid solution containing the tantalum is then crystallized into a salt and this tantalum containing salt is then reacted with pure sodium in order to reduce the tantalum containing salts to tantalum and to form salts with the non-tantalum containing elements. Water washing is then used to remove the salts and recover the tantalum which is subsequently subjected to one or more acid leachings to remove chemical impurities. The tantalum is then dried resulting in what is known as a basic lot powder. Typically, this basic lot(s) is subjected to a heat treatment or thermal agglomeration step and then passivated to obtain a powder cake that is subsequently ground up into a powder. A deoxidation step using oxygen getters, such as magnesium, is then performed. After the deoxidation step, the tantalum powder is generally subjected to an acid wash and dried. The powder is then pressed into a pellet and sintered for subsequent processing by capacitor anode manufacturers.

There is an interest by those skilled in the art to nitride valve metals, such as tantalum, with the belief that such nitriding can decrease the DC leakage in capacitor anodes formed from such nitrided tantalum. The current nitriding techniques primarily involve the use of nitrogen containing compounds or nitrogen gas during the deoxidation stage. This method has several disadvantages including the lack of uniform distribution of the nitrogen in the valve metal.

Accordingly, there is a desire to improve on the methods of nitriding valve metals as well as improving on the resulting product.

SUMMARY OF THE PRESENT INVENTION

A feature of the present invention is to provide processes to nitride valve metals, such as tantalum.

Another feature of the present invention is to provide a process which provides a more uniform distribution of the nitrogen throughout the valve metal.

A further feature of the present invention is to provide nitrided valve metals, such as tantalum.

An additional feature of the present invention is to provide a nitrided valve metal, such as tantalum, having high capacitance capability along with excellent flow properties and/or Scott density.

Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and obtained by means of the elements and combinations particularly pointed out in the written description and appended claims.

To achieve these and other advantages, and in accordance with the purpose of the present invention, as embodied and broadly described herein, the present invention relates to a process of preparing a nitrided valve metal comprising nitriding a valve metal powder at a sufficient temperature and pressure prior to the sintering phase of a heat treatment of the valve metal powder, or after the sintering phase of the heat treatment but prior to the deoxidation step, wherein the nitriding begins at an average valve metal temperature of from 200°C to 350°C.

The present invention further relates to a sintered nitrided valve metal having a nitrogen content of from 1,500 ppm to 4,000 ppm wherein all of said nitrided valve metal powder from the sintering has a uniform nitrogen distribution within 1,500 ppm or less. All ppm referenced herein are by weight.

The present invention also relates to a nitrided valve metal, such as tantalum, wherein at least a portion of the valve metal has pore sizes equal to or greater than 2 microns in size.

The present invention in addition relates to a nitrided tantalum powder having a nitrogen content of from 1,500 ppm to 4,000 ppm and a capacitance, when formed into a capacitor anode at 30 volts, of from 40,000 CV/g to 80,000 CV/g, wherein said nitrided tantalum powder has a flow of from 70 to 300 mg/s and has a Scott density of from 25 to 40 g/in^3.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide a further explanation of the present invention, as claimed.

The accompanying drawings, which are incorporated in and constitute a part of this application, illustrate several embodiments of the present invention and together with the description serve to explain the principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are graphs depicting the temperature and pressure conditions during a heat treatment, wherein tantalum powder was nitrided.

Figures 3 and 4 are graphs depicting pore size diameter of nitrided tantalum vs. Log Differential Intrusion (mL/g) and pore size diameter vs. Cumulative Pore Volume (mL/g).

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention relates to nitrided valve metals and processes for making nitrided valve metals.

For purposes of the present invention, valve metals include, but are not limited to, tantalum and niobium. Preferably, the valve metal is tantalum or niobium, and more preferably is tantalum.

The valve metal that is nitrided can be in any form and is preferably in the form of a powder. The powder can be any shape, such as flaked, nodular, or combinations thereof, and the like. Further, the powder can have any surface area and particle size and/or agglomerate size. For instance, the powder can have a BET surface area of from about 0.5 to about 10 m^2/g and more preferably from about 1 to about 3 m^2/g.

Furthermore, when the powder, such as tantalum, is formed into a capacitor anode, the capacitor preferably has a capacitance of from about 20,000 to about 80,000 CV/g, and more preferably from about 26,000 to about 64,000 CV/g when formed at 30 volts and a press density of 5.5 g/cc.

Preferably, the valve metal powder, especially tantalum, has a flow of from about 70 to about 300, and more preferably from about 80 to about 200 mg/s, as determined by the flow test recited in WO 99/61184, incorporated in its entirety by reference herein. Also, or alternatively, preferably the valve metal powder, especially tantalum, has a Scott Density of from about 25 to about 40, and more preferably, from about 26 to about 32 g/in^3.

The amount of nitrogen present in the valve metal powder can be any amount suitable for such applications as capacitor anodes. Preferably, the nitrogen content is from about 1,500 ppm to about 4,000 ppm. The inventor has found that amounts generally greater than about 4,000 ppm do not lead to any additional improvement in properties compared to lower amounts of nitrogen. Similarly, amounts lower than about 1,500 ppm nitrogen generally do not accomplish the desired improvements sought with nitrogen doping. Accordingly, the range of from about 1,500 ppm to about 4,000 ppm is beneficial, and more preferably the range of from about 2,000 ppm to about 3,000 ppm nitrogen.

The valve metal can also have a phosphorus content, such as from about 50 ppm to about 100 ppm. The valve metal can also have an oxygen content, such as from about 1,500 ppm to about 3,500 ppm.

In addition, the valve metal powder, preferably tantalum, has at least a portion of the pores with a pore size of 2 microns or greater leads to beneficial properties once a capacitor anode is made and impregnated, since such pore sizes permit the more uniform and complete impregnation with the counter electrode liquid.

As stated earlier, the process of nitriding the valve metal preferably begins with the basic lot powder of the valve metal. The following discussion uses tantalum as an example but it must be realized that the following discussion is applicable to any valve metal and the process conditions, such as temperature and time of heat treatment, varies depending upon the type of valve metal involved.

In the present process, the basic lot powder can be obtained by any processing techniques known to those skilled in the art. Such general processing techniques have been discussed above in the background of the invention and typically involve recovering the ore, crushing the ore, conducting solvent extraction to recover the tantalum in a salt form, and reducing the tantalum salt with sodium in order to form tantalum and other salts. These other salts are generally removed by water washing, and acid leaching can then be conducted to remove chemical impurities. The tantalum is then dried to obtain the basic lot. These above steps can be modified in any manner or alternative steps can be used in order to achieve what is known to those skilled in the art as a basic lot powder.

Once the basic lot is obtained, it is preferred (though, optional) for purposes of the present invention to conduct further processing of the tantalum powder or other valve metal prior to heat treatment. One preferred processing step before heat treatment is conducting water agglomeration as described in PCT Publication No. WO 99/61184 published December 2, 1999, incorporated in its entirety herein by reference. The tantalum powder in the form of a powder or powder cake, with or without the prior water agglomeration or other agglomeration procedures, can then be subjected to a heat treatment wherein the nitriding of the tantalum powder occurs.

For purposes of the present invention it is understood that heat treatment and thermal agglomeration refer to the same processing step which involves subjecting the tantalum powder or other valve metal powder to elevated temperatures generally in a furnace and generally under vacuum.

Preferably, in the heat treatment step and with reference to tantalum powder, if significant levels of hydrogen are present in the tantalum powder, such as on the order of greater than about 200 or 300 ppm hydrogen, then a degassing step is preferably conducted in order to substantially remove the hydrogen present. Typically, the degassing step will remove enough hydrogen from the tantalum powder so that after the degassing step, the amount of hydrogen present in the tantalum powder is below 50 ppm hydrogen and preferably below 40 ppm hydrogen gas.

Once the tantalum powder has been degassed (if needed), the heat treatment or thermal agglomeration of the tantalum powder can occur. With respect to tantalum, typically the sintering phase of the heat treatment occurs at a temperature of from about 1100° C to about 1500° C, which is the approximate average temperature reached on the surface of the powder in the furnace. Generally, the heat treatment at this temperature range occurs for about 10 minutes to about 2 hours, although other times can be used depending upon the desired properties. For purposes of the present invention, the heat treatment includes the time necessary to reach the sintering phase which generally causes some loss of surface area of the powder. Furthermore, the heat treatment typically occurs under vacuum and preferably at about .01 Torr or less. The nitriding of the tantalum powder occurs during heat treatment and prior to the deoxidation step.

The nitriding of the tantalum powder or other valve metal preferably occurs at a temperature of about 600° C or lower, and more preferably from about 250° C to about 600° C, and more preferably from about 300° C to about 400° C. Since the nitriding is preferably occurring at temperatures not above 600° C, it is preferred to conduct the nitriding where these temperatures are achievable, meaning, nitriding right before the sintering phase of heat treatment occurring at 1250° C - 1500° C or after this high temperature phase has occurred. In the present invention, the nitriding of the metal powder preferably occurs once the temperature of the metal powder has reached some stability and is not fluctuating significantly (e.g., not fluctuating by more than 50° C or so). Further, preferably the nitriding begins at a temperature of about 200° - 300° C to avoid the absorption of nitrogen in one location of the powder. Preferably, nitriding is started at a low temperature, like 200° C - 300° C, and then the temperature is ramped up at approximately 1° C to about 10° C per minute. Thus, a steady increase in temperature ensures that nitrogen absorption is uniform throughout the powder and further ensures that the temperature is substantially uniform for absorption, which can vary depending on powder and surface area, is reached for a sufficient time to permit absorption.

The nitriding of the tantalum powder can be accomplished with the use of a nitriding agent, such as nitrogen gas or a nitrogen containing gas or with nitrogen containing or generating compounds (e.g, TaN). Preferably, a nitrogen gas is used in this process. Generally, once the tantalum powder is at the preferred temperature range of from about 250° C to about 600° C, the nitriding process is preferably started. In the preferred embodiment, the nitrogen gas is introduced into the furnace under vacuum and the amount of nitrogen gas introduced is dependent upon the amount of nitrogen desired in the resulting nitrided powder and the amount of basic lot powder present in the furnace. In the Examples, it can be seen that various amounts of nitrogen were introduced in order to achieve various nitrogen contents in the powder. In view of the present invention, one skilled in the art can readily determine the amount of nitrogen to be introduced into the furnace for a desired amount of nitrogen in the final metal powder.

It is preferred that the nitrogen gas or other nitrogen generating techniques do not occur at temperatures above 600° C because the combination of nitrogen with tantalum is an exothermic reaction which generates heat and leads to an autocatalytic process which can be uncontrollable. This reaction leads to a non-uniformed distribution of the nitrogen in the basic lot powder.

Generally, during the nitriding process, the nitrogen is introduced into the furnace and is readily absorbed by the basic lot powder present in the furnace. Once the nitrogen gas has been absorbed, or prior to this step, the basic lot powder is subjected to the higher heat treatment phase or sintering phase of heat treatment described earlier. Once the desired heat treatment at high temperatures and the desired nitriding of the basic lot powder has occurred, the temperature is preferably substantially reduced in order to passivate the powder. Generally, the powder is in the form of a powder cake which is subsequently subjected to grinding. The powder can then be subjected to a deoxidation process. Any conventional deoxidation process can be used, such as with magnesium or any other oxygen getters. Once the deoxidation step and subsequent acid leaching is complete, the powder can be further processed in conventional manners, such as by pressing into pellets and sintering at desired temperatures which is dependent upon the desired capacitance and the type of valve metal being sintered. The sintered pellets can then be used as capacitor anodes using standard techniques known in the industry such as those set forth in U.S. Patent Nos. 4,805,074; 5,412,533; 5,211,741; and 5,245,514, and European Patent Application Nos. 0 634 762 A1, incorporated in their entirety herein by reference.

The nitriding of the valve metal during the heat treatment step is beneficial compared to other nitriding methods which typically occur during the deoxidation step. By nitriding during the heat treatment stage, a more uniform distribution of the nitrogen throughout the entire valve metal powder is achieved. One reason this occurs may be due to the fact that the nitriding occurs at an early stage of the metal processing and thereafter there are many other stages which involve subjecting the valve metal to high temperatures. These additional stages assist in uniformly distributing the nitrogen. Thus, the earlier the nitriding can occur, the more uniform distribution of the nitrogen throughout the valve metal can be achieved. In the examples, as can be seen, uniform nitrogen distribution was accomplished.

It is certainly possible and within the bounds of the present invention to conduct more than one nitriding step in order to achieve any amount of nitrogen content desired in the final product.

The present invention will be further clarified by the following examples, which are intended to be exemplary of the present invention.

EXAMPLES

Example 1

44 pounds of tantalum basic lot powder having the characteristics set forth in Table 1 were used. The basic lot tantalum powder was introduced into a furnace and placed under vacuum. A hydrogen degassing procedure was conducted by raising the temperature of the basic lot powder to about 745° C for one hour, and during this time the increase in pressure resulting from the hydrogen release was vented out using a vacuum. Thereafter, under vacuum, the basic lot powder temperature was further increased to about 1146° C for about 60 minutes and then the temperature of the basic lot powder was raised to about 1458° C for 30 minutes and then the temperature was reduced to about 350° C. Argon gas was introduced once the furnace cooled to about 1,000° C to aid in the cooling process. Once this lower temperature was reached, the argon gas was removed and nitrogen gas was introduced into the vacuum by pumping out and replacing the argon with nitrogen gas at a pressure of about 80 Torr. During this nitrogen addition, the temperature of the basic lot powder was increased to about 500° C at a rate increase of 1° C per minute and the pressure of the nitrogen gas decreased to about 1 Torr or less because the tantalum was absorbing the nitrogen. Once the nitrogen was absorbed, the furnace was then backed filled with argon and the powder was permitted to cool. Figure 1 plots this procedure.

Upon measurement, the basic lot powder had a nitrogen content of about 1,500 ppm. Figure 1 reflects the temperature and pressure changes as well as the point of nitrogen introduction during the heat treatment.

Example 2

A basic lot tantalum powder (72 lbs.-36 lbs. of this tantalum was doped with 50 ppm P) similar to that used in Example 1 was subjected to a heat treatment like in Example 1, wherein the basic lot powder was subjected to a hydrogen degassing procedure by raising the temperature of the basic lot powder to about 750° C for about 1 hour and 15 minutes. During this time, the release of hydrogen gas was vented under vacuum. Once the vacuum level reaches 10 microns or lower, the temperature of the basic lot powder was then allowed to cool down to about 350° C wherein about 80 Torr of nitrogen gas was introduced into the furnace. Like in Example 1, the nitrogen gas was essentially fully absorbed by the tantalum powder and there was a temperature increase during this time of about 60° C. Once the nitriding was finished, the furnace chamber was evacuated to 10 microns or less and then the temperature of the basic lot powder was then raised to about 1186° C for about an hour and a half and then raised even higher to about 1350° C for 30 minutes (sintering phase of heat treatment) and thereafter the temperature of the basic lot tantalum powder was allowed to cool off for further processing. Figure 2 plots this procedure.

Example 3

The powders from Examples 1 and 2 were then processed as follows:

Heat treated material which was in the form of cakes was crushed and screened using 70 mesh (US Sieve) screen. The –70 mesh powder was blended with magnesium. Magnesium content was 0.75% by weight. Magnesium blended tantalum powder was deoxidized by reacting at 850C. This deoxidation step was conducted to lower the oxygen content of the tantalum powder to reasonable level. The deoxidized tantalum powder was then treated with nitric acid, hydrofluoric acid and deionized water to remove the residual magnesium and the magnesium oxide generated during the deoxidation process. Acid treated powder was further rinsed with deionized water until a conductivity of less than 10 micromhos/cm was attained in the DI water. The rinsed tantalum powder was dried using a vacuum dryer. A representative sample of the dried powder was taken and analyzed for physical, chemical, and electrical properties of the powder. The results are shown in the Tables 1, 2, and 3. The electrical properties were evaluated using the following procedure:

[1] Anode Fabrication:
    (a) N = 16 anodes per sample
    (b) Diam = 0.1235"
        Length = 0.1021"
        Powder Wt = 100 mg
        Dp = 5.0 g/cc

[2] Anode Sintering (NRC Furnace):
    (a) 1 Sinters
        1430° C * 30' (10° C per minute ramp)

[3] 100V Ef Evaluation:
    (a) Anodization:
        (1) One Formation
            N = 8 anodes (one tree) per sample
            (1) tree/sample + standards
        (2) Electrolyte; (.1% H_3PO_4 @ 90° 3.08 mmho)
        (3) Constant current density: (75 ma/g)
        (4) Terminal Voltage = 100.0 VDC +/- 0.03
        (5) Terminal Voltage Time = 180 min -0/+5 min
        (6) 25° C soak for 30 min
        (7) 100° C oven for 30 min
    (b) DC Leakage:
        (1) Charge E = 70.0 +/- .02
        (2) Charge Time = 30 sec & 120 sec
        (3) DCL Test Electrolyte = 10% H_3PO_4 @ 21° C

(c) Capacitance/DF:
- (1) Capacitance Test Electrolyte = 18% $H2SO4$ @ 21° C
- (2) Bias = 2.5 VDC
- (3) Frequency = 120 Hz
- (4) Series Capacitance
- (5) GenRad # 1658

Example 4

A sample was prepared using basic lot tantalum powder described in Table 9. Sample was prepared by soaking 60 pounds of tantalum with 34% of deionized water containing phosphorous dopant solution to provide 100 ppm by weight of phosphorous. The powder was soaked for 16 hours. Soaked powder was transferred to Teflon coated stainless steel trays and additional 3% of deionized water was added. The wet powder was vibrated for eight to ten minutes using the vibrating table. After vibrating, the trays were allowed to sit for at least sixty minutes for any water to separate. Any water which separated was decanted. Afterwards the drying trays were transferred to a vacuum dryer. The commercial vacuum dryer was purchased from STOKES VACUUM Inc. The model number is 338J. The material in the stainless steel trays was dried for approximately 14 hours at about 195° F and 50 torr pressure. The dried tantalum powder was then transferred to a tantalum tray for heat treatment. The heat treatment was conducted at approximately 1309° C for about 30 minutes. The cakes were then transferred to a batch can for milling and were milled and screened using 70 mesh (US Sieve) screen. –70 mesh portion of the material was deoxidized using 2% magnesium at 850 °C and acid leached using nitric acid, hydrogen peroxide and deionized water. Powder was further rinsed with DI water until the conductivity is lowered to less than 5 micromhos/cm. Rinsed powder was dried in a vacuum dryer. Samples were deoxidized again, to lower the oxygen, using 2% magnesium at 850° C and acid leached, rinsed and dried as described above. The final product was analyzed and the data is shown in Table 4 and 9.

Electrical evaluation was conducted using the following procedure.

[1] Anode Fabrication:
- (a) Haberer Press--
  - (1) N = 16 anodes per sample
  - (2) non-lubed powder
  - (3) size - 0.1545" dia x .1225" length
  - (4) Dp = 5.0 g/cc
  - (5) powder wt = 188 mg

[2] Anode Sintering:
- (a) NRC Furnace;
  - 1335° C * 10 ("A" ramp)

[3] 30V Ef Evaluation:
- (a) Anodization:
    - (1) N = 8 anodes (one tree) per sample
    - (2) Electrolyte; E251 Test Electrolyte (.06% $H3PO4$ @ 83°, 2.86 mmho)
    - (3) Constant current density: E251 Test current (337.5 ma/g)
    - (4) Terminal Voltage = 30.0 VDC +/- 0.03
    - (5) Terminal Voltage Time = 300 min -0/+5 min
    - (6) Soak 25° for 30 minutes
    - (7) 100° C oven for 30 minutes
- (b) DC Leakage:
    - (1) Charge E = 21.0 +/- .02
    - (2) Charge Time = 30 & 120 sec
    - (3) DCL Test Electrolyte = 10% $H3PO4$ @ 21° C
- (c) Capacitance/DF:
    - (1) Capacitance Test Electrolyte = 18% $H2SO4$ @ 21° C
    - (2) Bias = 2.5 VDC
    - (3) Frequency = 120 Hz
    - (4) Series Capacitance
    - (5) GenRad # 1658

Final properties of the tantalum powders are set forth in Tables 4, 5, and 9.

Example 5

In this example, about 45 lbs. of basic lot tantalum powder per lot were nitrided as in Example 4 except the final temperature of the powder was about 1300° C for about 30 minutes. The characteristics of the resulting nitrided tantalum are set forth in Tables 4 and 5. Figure 3 reflects the pore size distribution of a pressed and sintered tantalum pellet and Figure 4 reflects the cumulative pore volume for each pore size.

Example 6

72 pounds of basic lot tantalum powder were doped with nitrogen for a target nitrogen content of 1500 ppm. In this process, the powder was heated to 740° C followed by hydrogen degassing and then the powder was cooled down to about 325° C. At this point, nitrogen gas was introduced in the same manner as in Example 1. Following nitrogen doping, the samples were removed to determine whether the nitrogen doping distribution was uniform for all of the trays containing tantalum powder in the furnace. The particulars of doping with nitrogen and other parameters are set forth in Table 6. Table 7 (run number 5) also sets forth another experiment involving nitrogen doping for a variety of samples in the furnace with the target value of 2,500 ppm nitrogen in the final product.

As a comparison, tantalum powder was nitrided during the deoxidation stage. The nitrogen doping amount was higher but this was done in order to ensure nitrogen was absorbed in all tray samples. Details are set forth on Table 8.

As can be seen from Tables 6 and 7, the amount of nitrogen content on average was very close to the target value in each instance and the overall difference between the various trays was within acceptable parameters. When nitriding occurred during the deoxidation stage, the non-uniform nitrogen distribution from tray to tray was observed as can be seen in Table 8. In more detail, there was large differences in absorbed nitrogen amounts from tray to tray. Where nitriding during heat treatment caused a variation of about 1,000-1,500 ppm, nitriding during deoxidation caused a variation over 20,000 ppm.

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

Table 1

Used HP410 basic lot blend. 36 lbs. From HP410-B-121828 and 36 lbs. From HP410-B-121829. 36 pounds was processed without "P" and the other 36 pounds was doped with 50 ppm "P" using NH4PF6. Powder was heated to 740 °C followed by degas, cool down to 325 °C and nitrogen was introduced. 1500 ppm AIM. This is heat treated for 90 min @1180 ° C followed by 30 min @ 1350 °C (SPC: 1447C)

	8187-11-B	8187-11-NM2
	Basic Lot	Finished product
HT set point		30 min @ 1350C
FSS (microns)	0.89	2.54
Scott (gms/inch3)	18.7	31.0
BET (m2/gm)	1.00	0.59
Na (ppm)	6	2
K (ppm)	11	4
P (ppm)	48	4
C (ppm)	12	24
O (ppm)	2822	1670
N (ppm)	29	2326
H (ppm)	557	36
Si (ppm)	240	19
Fe (ppm)	4	4
Ni (ppm)	5	10
Cr (ppm)	4	4
Nb (ppm)	24	24
Ti (ppm)	4	4
Mn (ppm)	4	4
Sn (ppm)	4	4
Ca (ppm)	4	4
Al (ppm)	4	4
Mo (ppm)	4	4
W (ppm)	24	24
Zr (ppm)	4	4
Mg (ppm)	4	4
B (ppm)	3	3
Co (ppm)	4	4
Cu (ppm)	4	4
Screens		
+60		2.4
60/100		14.7
100/200		26.4
200/325		15.2
325/400		9.0
-400		32.3
FLOW (mg/sec)		163
Crush Str.		26.0 lbs
1480C 50V Cap		25970
DCL (nA/CV)		0.07
Fliers		0/8
Shrinkage		3.3
Sinter Density		5.4

Press Density 5.0 g/cc

Table 2 (Example 1)

Used HP 410 basic lot blend. 36 lbs. From HP 410-B-121828 and 36 lbs. from HP410-B-121829. 36 pounds was processed without "P" and the other 36 pounds was doped with 50 ppm "P" using NH_4PF_6. Powder was heated to 740 °C followed by degas, cool down to 325 °C and nitrogen was introduced. 1500ppm AIM. This is heat treated for 90 min @ 1180 °C followed by 30 min at 1350 °C (SPC: 1447C).

	8187-11-B	8187-11-NM2
	Basic Lot	Finished Product
HT (SPC)		1447 C
FSS (microns)	0.89	2.54
Scott (gms/inch3)	18.7	31.0
BET (m2/gm)	1.00	0.59
C (ppm)	12	24
O (ppm)	2822	1670
N (ppm)	29	2326
H (ppm)	557	36
Screens		
+60		2.4
60/100		14.7
100/200		26.4
200/325		15.2
325/400		9.0
-400		32.3
FLOW (mg/sec)		163
1430C 100V C		
Cap (CV/gm)		23,829
DCL (nA/CV)		0.33
Shrinkage		0.1
Sinter Density		5.1

Table 3 (Example 2)

	8187-11-B	8187-19-NM
	Basic Lot	Final Product
HT (SPC)		1458 C
FSS (microns) (mod)	0.89	2.35
Scott (gms/inch3)	18.7	29.4
BET (m2/gm)		0.37
C (ppm)	12	23
O (ppm)	2822	1959
N (ppm)	29	1333
H (ppm)	557	50
Screens		
+60		0.0
60/100		7.3
100/200		28.2
200/325		18.7
325/400		10.2
-400		35.5
1430C 100V Cap		
Capacitance (CV/gm)		24,885
DCL (nA/CV)		0.24
Shrinkage		-0.6
Sinter Density		4.8

Table 4

Physical, Chemistry Properties of Nitrided Powder

	8280-66-nm2a	8280-67-nm2a	8280-68-nm2a	Average
Modified FSS (microns)	2.91	2.39	2.32	2.54
Scott (gms/in3)	28	27.8	27.9	27.9
BET	1.11	1.03	1.15	1.10
C (ppm)	60	56	57	58
O (ppm)	3288	3058	2978	3180
N (ppm)	2509	2379	2483	2457
H (ppm)	71	81	87	79.7
Si (ppm)	5	5	4	4.7
Ni (ppm)	17	4	4	8.3
Fe (ppm)	4	4	4	4.0
Cr (ppm)	4	4	4	4.0
Cb (ppm)	24	24	24	24.0
Ti (ppm)	4	4	4	4.0
Mn (ppm)	4	4	4	4.0
Sn (ppm)	4	4	4	4.0
Ca (ppm)	4	4	4	4.0
Al (ppm)	4	4	4	4.0
Mo (ppm)	4	4	4	4.0
W (ppm)	24	24	24	24.0
Zr (ppm)	4	4	4	4.0
Mg (ppm)	5	5	10	6.7
B (ppm)	1	1	1	1.0
Co (ppm)	4	4	4	4.0
Cu (ppm)	4	4	4	4.0
Na (ppm)	6	4	5	5.0
K (ppm)	29	26	28	27.7
Screens				
+60	0	0	0	0.0
-60/+100	23.4	23.7	30.5	25.87
-100/+200	33.1	35.2	33.2	33.83
-200/+325	15.6	14.6	12.6	14.27
-325/+400	8.2	7.8	6.8	7.60
-400	19.7	18.7	16.9	18.43
Flow (mg/sec)	97.4	103.4	103.3	101.4

mtrack				
per 10	27.72	29.83	22.33	26.63
per 50	118.31	119.08	109.43	115.61
per 90	261.04	260.8	265.11	262.32
SA	0.102	0.094	0.127	0.11

Table 5

Electrical Properties of Nitrided Powder

	8280-66-NM2A	8280-67-NM2A	8280-68-NM2A	Average
Sintering Temp.				
1335C 30V	36.3	35.9	41.0	37.7
Cap (cv/gm)	67,726	68,686	68,898	68,437
DCL (na/cv)	0.31	0.27	0.36	0.32
Fliers	0	1	0	0.33
Sint. Den.	5.20	5.17	5.18	5.18
Shrinkage	1.68	1.81	1.61	1.70
Sintering Temp.				
1265 °C 30V				
Cap (cv/gm)	70,266	71,198	71,769	71,077
DCL (na/cv)	0.30	0.35	0.26	0.30
Fliers	0	0	0	0.00
Sint. Den.	4.94	4.92	4.95	4.94
Shrinkage	0.05	0.11	0.16	0.11
Sintering Temp.				
1335 °C 60V				
Cap (cv/gm)	53,802	54,719	54,495	54,338
DCL (na/cv)	0.53	0.38	0.42	0.44
Fliers	0	0	0	0.00
Sint. Den.	5.19	5.17	5.18	5.18
Shrinkage	1.68	1.81	1.61	1.70
Sintering Temp.				
1265 °C 60V				
Cap (cv/gm)	55,541	56,460	56,370	56,124
DCL (na/cv)	0.63	0.44	0.43	0.50
Fliers	0	1	0	0.33
Sint. Den.	4.94	4.92	4.95	4.94
Shrinkage	0.05	0.11	0.16	0.11

Press Density in each case was 5.0 g/cc.

Table 6

72 pounds of HP410 basic lot (C410-S-128793) was doped with nitrogen to an aim value of 1500 ppm. Powder was heated to 740 °C followed by degas, cool down to 325 °C and nitrogen was introduced.

	Tray #	Position	Oxygen	Nitrogen
8187-10-1T	Tray 1	Top	3848	598
8187-10-1M	Tray 1	Middle	4467	2172
8187-10-1B	Tray 1	Bottom	4498	1749
8187-10-2T	Tray 2	Top	3924	1056
8187-10-2M	Tray 2	Middle	4055	1539
8187-10-2B	Tray 2	Bottom	4567	1570
8187-10-3T	Tray 3	Top	3598	938
8187-10-3M	Tray 3	Middle	4386	1586
8187-10-3B	Tray 3	Bottom	4605	1328
8187-10-4T	Tray 4	Top	3700	719
8187-10-4M	Tray 4	Middle	4041	696
8187-10-4B	Tray 4	Bottom	4269	673
8187-10-5T	Tray 5	Top	3794	813
8187-10-5M	Tray 5	Middle	4207	1689
8187-10-5B	Tray 5	Bottom	4402	2297
8187-10-6T	Tray 6	Top	3662	1300
8187-10-6M	Tray 6	Middle	4399	2382
8187-10-6B	Tray 6	Bottom	4424	1612
8187-10-7T	Tray 7	Top	3671	1279
8187-10-7M	Tray 7	Middle	4321	2084
8187-10-7B	Tray 7	Bottom	4419	1702
8187-10-8T	Tray 8	Top	3926	1074
8187-10-8M	Tray 8	Middle	4228	679
8187-10-8B	Tray 8	Bottom	4692	554
8187-10-NBZ		Blend	4165	1420
		Avg.	4171	1329

Ta Powder weight: 72 pounds
Nitrogen aim Value: 1500 ppm
Nitrogen Flow rate: 3 liters/min
Nitrogen addition Time: 16 minutes
Total pressure: 134 torr
Nitrogen Doping Temp.: 325C Ramp up @ 1C/min.
Total Nitrogen absorption time: 240 minutes
Final Temperature achieved: 498 °C

Table 6 (cont.)

Nitrogen Analysis for 8187-10-H run

		Front		Rear
Tray #1	Top	598		813
	Middle	2172		1689
	Bottom	1749		2297
Tray #2	Top	1056		1300
	Middle	1539		2382
	Bottom	1570		1512
Tray #3	Top	938		1279
	Middle	1586		2084
	Bottom	1328		1702
Tray #4	Top	719		1074
	Middle	696		679
	Bottom	573		554
	Average	1210		1447
			1329	
	Blend		1420	

Table 7

72 pounds of HP410 basic lot (C410-S-128793) was doped with nitrogen to an aim value of 2500 ppm. PLC crashed during the cool down phase. The run was aborted and rerun on 5/11/99. Powder was heated to 740 °C followed by degas, cool down to 325 °C and nitrogen was introduced.

	Tray #	Position	Carbon	Oxygen	Nitrogen	Hydrogen
8187-2-1T	Tray 1	Top	45	6612	1076	44
8187-2-1M	Tray 1	Middle	28	5705	2278	29
8187-2-1B	Tray 1	Bottom	38	6136	2335	30
8187-2-2T	Tray 2	Top	48	6247	2314	33
8187-2-2M	Tray 2	Middle	28	5646	2346	27
8187-2-2B	Tray 2	Bottom	42	5136	2213	23
8187-2-3T	Tray 3	Top	51	5881	2002	38
8187-2-3M	Tray 3	Middle	29	5618	1742	26
8187-2-3B	Tray 3	Bottom	35	5853	1838	30
8187-2-4T	Tray 4	Top	56	5936	946	37
8187-2-4M	Tray 4	Middle	26	5481	664	27
8187-2-4B	Tray 4	Bottom	34	5869	681	25
8187-2-5T	Tray 5	Top	53	6463	1467	43
8187-2-5M	Tray 5	Middle	33	5706	4237	27
8187-2-5B	Tray 5	Bottom	39	5987	3464	27
8187-2-6T	Tray 6	Top	44	5784	2478	38
8187-2-6M	Tray 6	Middle	50	5743	3240	21
8187-2-6B	Tray 6	Bottom	39	6035	3259	16
8187-2-7T	Tray 7	Top	42	6131	2319	36
8187-2-7M	Tray 7	Middle	28	5708	2189	26
8187-2-7B	Tray 7	Bottom	35	6027	2161	26
8187-2-8T	Tray 8	Top	58	5848	1364	31
8187-2-8M	Tray 8	Middle	27	5624	842	30
8187-2-8B	Tray 8	Bottom	33	5848	670	19
8187-2-NB		Blend	36	5821	2407	21
		Avg.	39	5922	2001	30

Ta Powder weight: 70 pounds
Nitrogen aim Value: 2500 ppm
Nitrogen Flow rate: 3 liters/min
Nitrogen addition Time: 24 minutes
Total pressure: 205 torr
Nitrogen Doping Temp.: 325C Ramp up @ 1C/min.
Total Nitrogen absorption time: 176 minutes
Final Temperature achieved: 489 °C

Table 7 cont.

Nitrogen Analysis for 8187-2-H run

		Front		Rear
Tray #1	Top	1076		1467
	Middle	2278		4237
	Bottom	2335		3464
Tray #2	Top	2314		2478
	Middle	2346		3240
	Bottom	2213		3259
Tray #3	Top	2002		2319
	Middle	1742		2189
	Bottom	1838		2161
Tray #4	Top	946		1364
	Middle	664		842
	Bottom	581		670
	Average	1695	2001	2308
	Blend		2407	

Table 8

Nitriding Run 2500ppm Target.

All batches were deoxed using 0.75% Magnesium @ 850 °C (100min soak + 60min vacuum). Nitriding parameters 450 °C with 5000 ppm set point @ 2.5 Liters/min. Flow rate. No pressure raise during nitrogen doping.

	After deox and acid leaching	
Sample	Nitrogen (ppm)	Oxygen (ppm)
8030-95-M1	938	2093
8030-95-M2	14670	1883
8030-95-M3	20330	2429
8030-95-M4	19050	2466
8030-95-M5	27190	1991
8030-95-M6	17740	1767
8030-95-M7	10920	2067
8030-95-M8	5621	1773
8030-95-M9	2909	2373
8030-95-M10	2352	2401
8030-95-M11	1546	2127
8030-95-M12	1176	2052
8030-95-M13	630	2870
8030-95-M14	539	2191

Non-uniform nitrogen observed when nitrogen doping was conducted during its deox process.

Table 9

Process
Basic lots were soaked with 34% water.
Water agglomerated with 37% water.
Materials was heat-treated at 1309 spc anode temperature.
Nitrogen was doped before heating up.
Target for Nitrogen doping is 2500 ppm.

	Basic lots	Finished Material
	8280-66-b	8280-67-nm2a
Modified FSS (microns)	0.37	2.39
Scott (gms/in3)	12.3	27.8
BET	2.74	1.03
C (ppm)	46	56
O (ppm)	8682	3058
N (ppm)	43	2379
H (pm)	1482	81
Screens		
+60		0
-60/+100		23.7
-100/+200		35.2
-200/+325		14.6
-325/+400		7.8
-400		18.7
Flow		103.4
1335C 30V		
Cap (cv/gm)		68,686
DCL (na/cv)		0.27
Fliers		1
Sint. Den.		5.17
Shrinkage		1.81

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process of preparing a nitrided valve metal comprising nitriding a valve metal powder at a sufficient temperature and pressure prior to the sintering phase of a heat treatment of the valve metal powder, or after the sintering phase of the heat treatment but prior to the deoxidation step, wherein the nitriding begins at an average valve metal temperature of from 200°C to 350°C.

2. The process of claim 1, wherein said nitriding is accomplished with nitrogen gas.

3. The process of claim 1, wherein said nitriding is accomplished with at least one nitrogen-generating compound.

4. The process of claim 1, wherein said nitriding results in said valve metal having a nitrogen content of from 1,500 ppm to 4,000 ppm.

5. The process of claim 1, wherein said heat treatment comprises heating the valve metal to a temperature of from 1,250°C to 1,500°C for a period of time of from 10 minutes to 2 hours, wherein said valve metal is tantalum.

6. The process of claim 1, wherein said nitriding occurs at a temperature of from 250°C to 600°C.

7. The process of claim 1, wherein prior to said nitriding, said valve metal is hydrogen degassed.

8. The process of claim 1, wherein said nitrided valve metal, after nitriding, is subjected to at least one passivation step, at least one deoxidation step, and at least one sintering step.

9. The process of claim 1, wherein said valve metal is tantalum.

10. The process of claim 1, wherein said valve metal is niobium.

11. The process of claim 1, wherein the average valve metal temperature is increased at a rate of less than 10°C per minute until nitriding is complete.

12. A sintered nitrided valve metal having a nitrogen content of from 1,500 ppm to 4,000 ppm wherein all of said nitrided valve metal powder from the sintering has a uniform nitrogen distribution within 1,500 ppm or less.

13. The nitrided valve metal of claim 12, wherein said valve metal is tantalum.

14. The nitrided valve metal of claim 12, wherein said valve metal is niobium.

15. A nitrided tantalum powder having a nitrogen content of from 1,500 ppm to 4,000 ppm and a capacitance, when formed into a capacitor anode at 30 volts, of from 40,000 CV/g to 80,000 CV/g, wherein said nitrided tantalum powder has a flow of from 70 to 300 mg/s and has a Scott density of from 25 to 40 g/in^3.

16. A capacitor anode comprising the tantalum powder of claim 13.

17. A capacitor anode comprising the niobium powder of claim 14.

18. The sintered nitrided valve metal of claim 12, wherein said nitrided valve metal powder comprises pore sizes of at least 2 microns.

19. The sintered nitrided valve metal of claim 13, wherein said nitrided valve metal powder comprises pore sizes of at least 2 microns.

20. The sintered nitrided valve metal of claim 14, wherein said nitrided valve metal powder comprises pore sizes of at least 2 microns.

21. A capacitor anode comprising the nitrided tantalum powder of claim 15.

22. The nitrided tantalum powder of claim 15 having pore sizes of at least 2 microns.

23. The nitrided tantalum powder of claim 15, wherein said Scott Density is from 26 to 32 g/in^3.

24. The nitrided tantalum powder of claim 15, wherein said nitrogen content is from 2,000 ppm to 3,000 ppm nitrogen.

25. The nitrided tantalum powder of claim 15, wherein said powder has a BET surface area of from 1 to 3 m^2/g.

26. The nitrided tantalum powder of claim 15, wherein said nitrided tantalum powder has a BET surface area of from 0.5 to 3 m^2/g.

27. The nitrided valve metal of claim 12, wherein said nitrided valve metal powder has a BET surface area of from 0.5 to 10 m^2/g.

28. The nitrided tantalum powder of claim 15, further comprising a phosphorus content, an oxygen content, or both.

29. The nitrided tantalum powder of claim 15, further comprising a phosphorus content of from 50 ppm to 100 ppm, an oxygen content of from 1,500 ppm to 3,500 ppm, or both.

30. The nitrided tantalum powder of claim 15, further comprising a BET surface area of from 0.5 to 10 m^2/g.

31. A process for preparing a nitrided valve metal substantially as hereinbefore described with reference to the Examples, and accompanying Tables and Figures.

32. A sintered nitrided valve metal substantially as hereinbefore described with reference to the Examples, and accompanying Tables and Figures.

33. A nitrided tantalum powder substantially as hereinbefore described with reference to the Examples, and accompanying Tables and Figures.

DATED this 26th day of November 2004

CABOT CORPORATION

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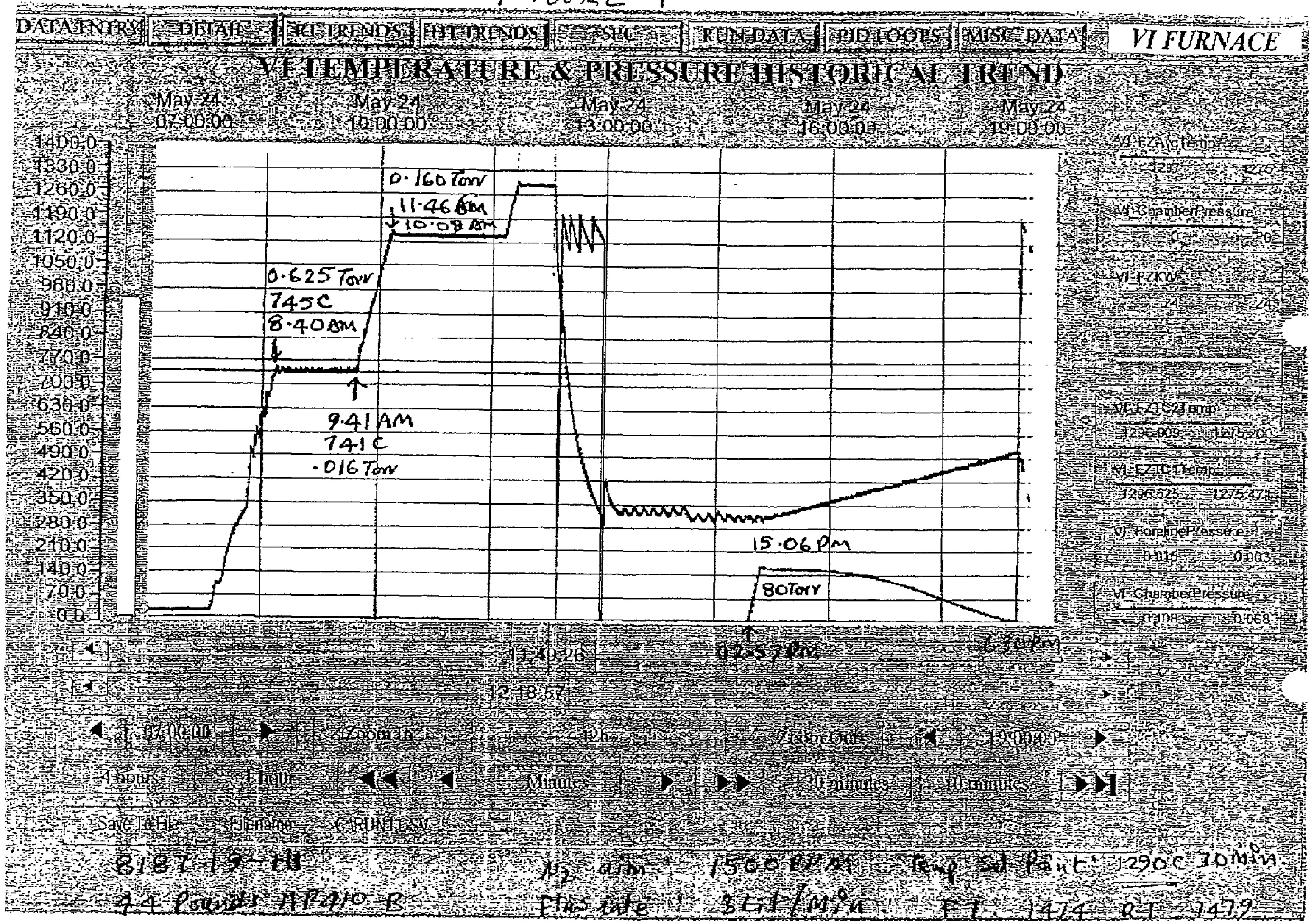
P21852AU00 KJS/JPF/VRH

FIGURE 1



8187-19-HI

74 Pounds AP2410 B

N_2 atm 1500 PPM Temp Set Point: 1290C 30Min

Flow rate: 3Lit/Min. FT: 1474 RT: 1479

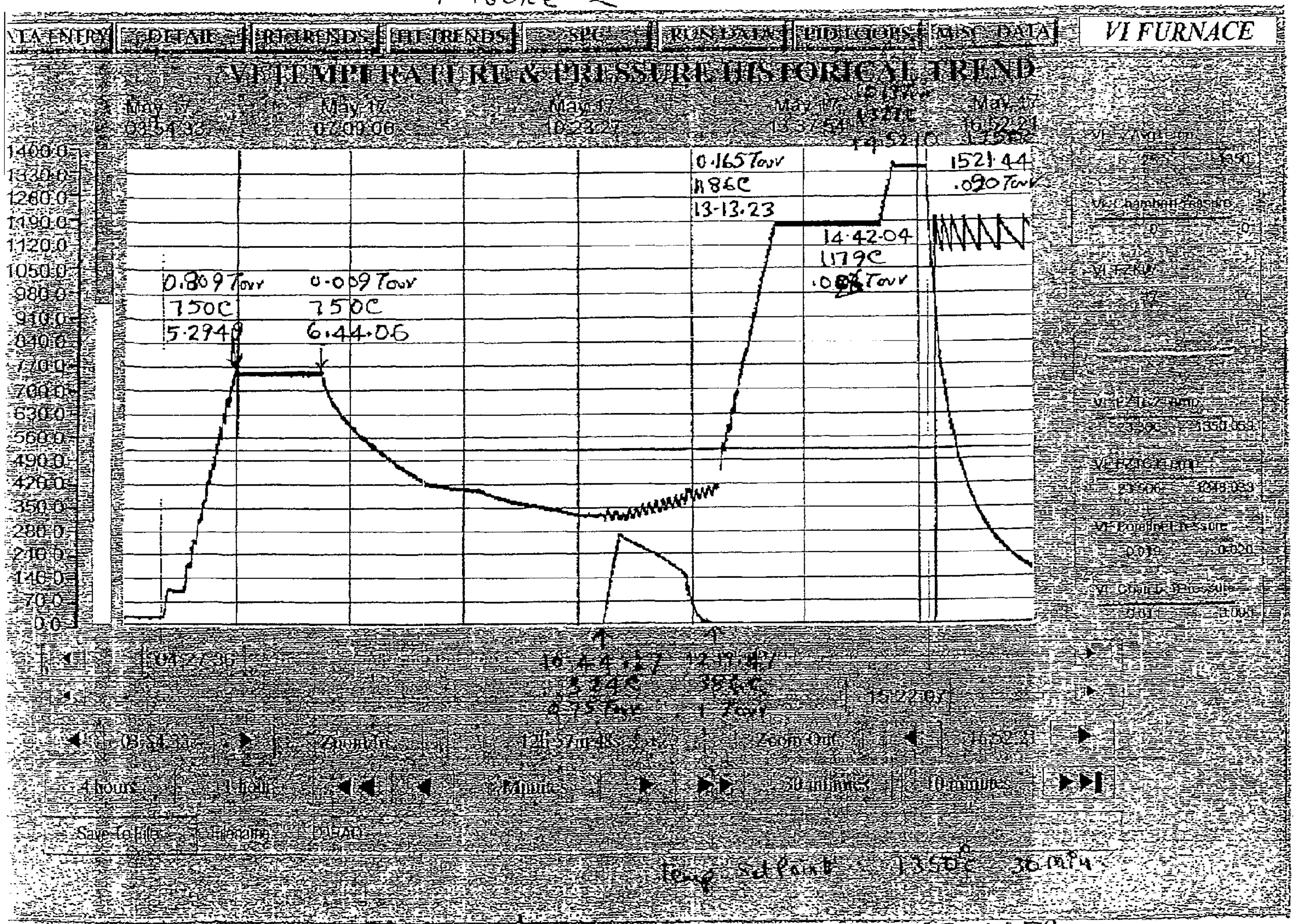
HT 90 mts. @ 1140C
30mts @ 1280C

FIGURE 1.

FB 1439 RB: 1441

AVG: 1458C

FIGURE 2

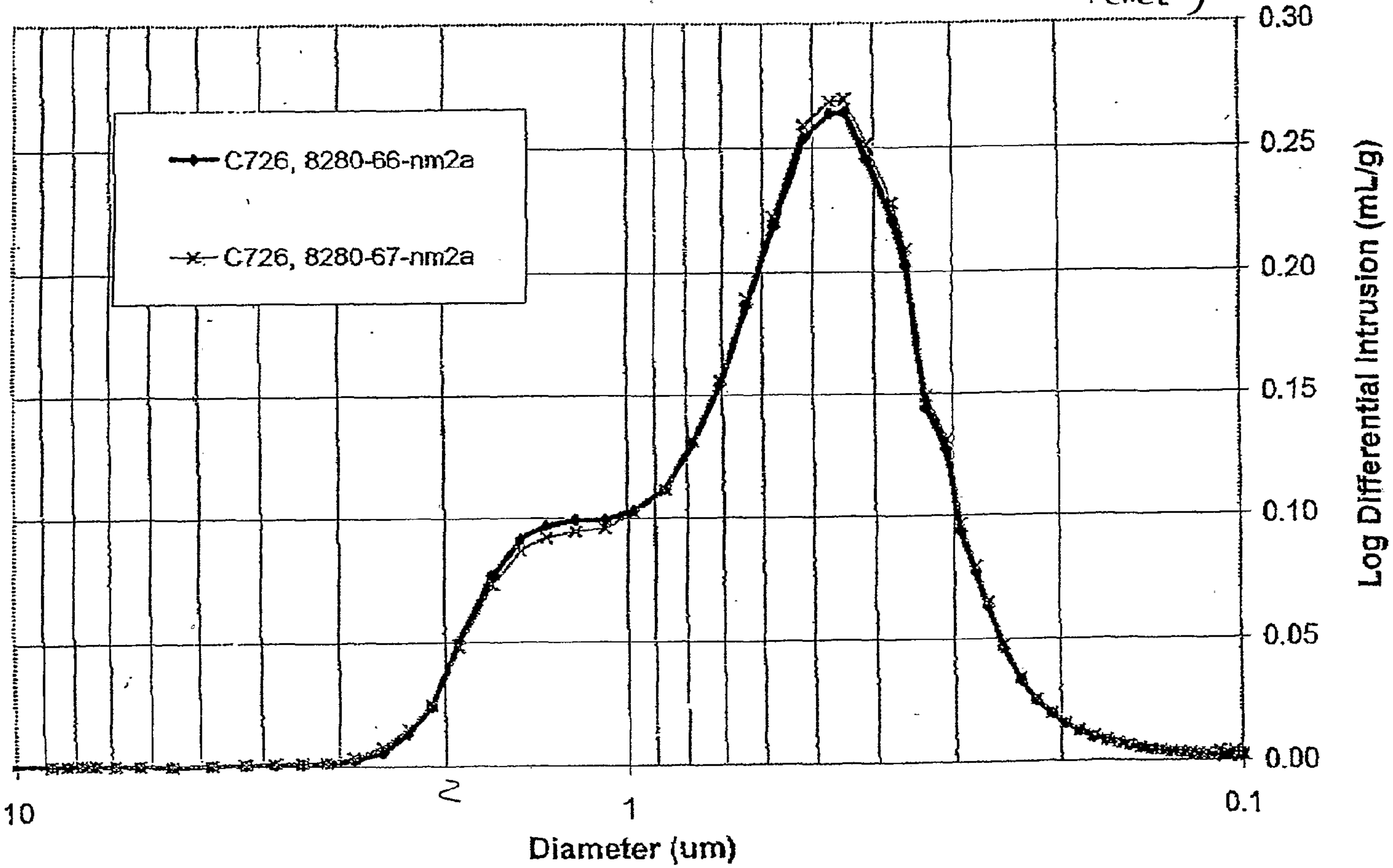


8187-11-H1 36lb. without P
8187-11-H2 36lb. with 50ppm 'P'.

36 lbs N_2
36 lbs N_2 = 72 lbs N_2

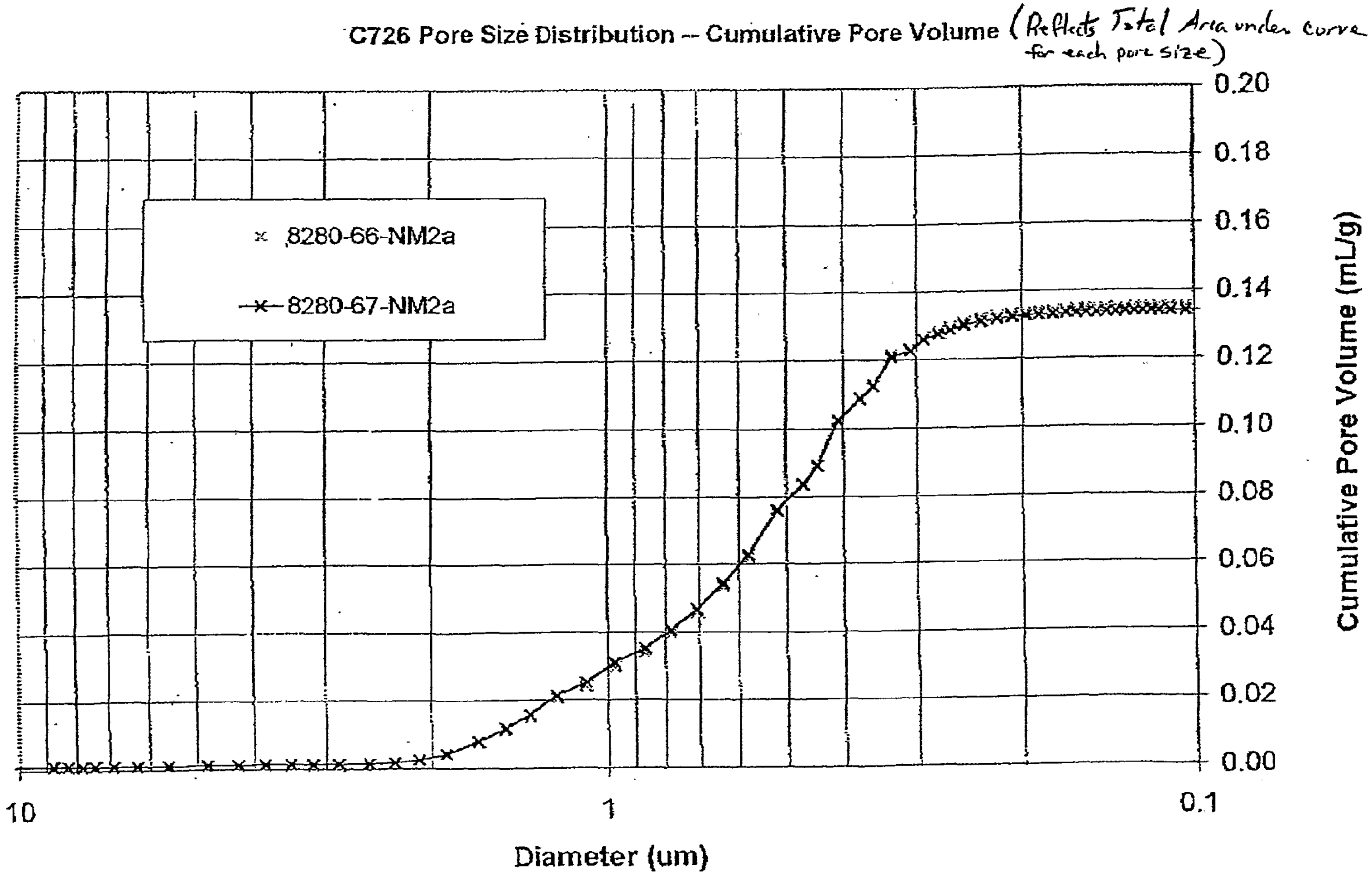
FT : 1459 RT 1459
FB : 1434 RB 1435
Avg : 1447C

FIGURE 3



C726 Pore Size Distribution -- Differential Intrusion (dV/dlogD) (of Pressed and Sintered Pellet)

FIGURE 4


C726 Pore Size Distribution -- Cumulative Pore Volume (Reflects Total Area under curve for each pore size)
8280-66-NM2a
8280-67-NM2a
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Cumulative Pore Volume (mL/g)
10
1
0.1
Diameter (um)