MLM-2465(OP)

MASTER

Conf-771012--3

CHARACTERIZATION OF TITANIUM METAL POWDER BY PULSED NMR

A. Attalla

Mound Facility*
Miamisburg, Ohio 45342

ABSTRACT

Moisture absorption as a function of surface area in titanium metal powders was studied by pulsed NMR. Wet samples were air-dried for 16 days under normal laboratory conditions (20-22°C, 40-60% relative humidity) and the moisture contents were compared with those of vacuum-dried (200°C, 1.33 mPa) samples and vacuum-dried samples exposed to 50% relative humidity. For one sample, the drying efficiency of 100°C as compared to 200°C, as well as the moisture absorption capacity as a function of time, was also studied. The moisture, hydride hydrogen (TiH_2), and oxygen contents of titanium metal powders were found to be functions of surface area. Moisture absorbed was a linear function and hydrogen and oxygen were exponential functions of surface area. Titanium metal powder absorbs an equilibrium value of moisture (~0.60 wt %) within one hour of exposure to 50% relative humidity. The drying of titanium metal powder was found to be as effective at 100°C as at 200°C.

*Mound Facility is operated by Monsanto Research Corporation for the Department of Energy under Contract No. EY-76-C-04-0053.

INTRODUCTION

An important constituent of pyrotechnic devices manufactured at Mound Facility is titanium metal powder [1]. The physical and chemical behavior of this powder is highly influenced by its previous history. One high-surface area sample, QC 1766, for example, ignited when exposed to the atmosphere after vacuum drying at 200°C for 72 hr. Thus, synthesis batch, surface area, and heat treatment all affect the behavior of the powder with regard to moisture absorption and reaction with oxygen. It is the purpose of this investigation to study the effects of heat treatment and particle size (surface area) on the absorption of moisture by two synthesis batches of titanium metal powder. The measures of these effects are: amount of hydrogen remaining after drying; amount of moisture absorbed after drying; the rate of absorption of moisture after drying; and the degree of correlation of surface area with moisture, oxygen, and hydrogen content of the titanium metal powders.

EXPERIMENTAL

Six titanium metal powder samples were selected for their wide range of surface areas (Table 1). The samples were washed repeatedly in deionized, distilled water and centrifuged to remove foreign, soluble matter. The centrifuged powders were air-dried for 16 days in protected, shallow, stainless steel pans on the laboratory bench (Treatment I). The humidity in the laboratory was monitored with a Bacharach humidity recorder. The humidity varied uniformly between 40 and 60% during the drying period.

Samples QC 1762 and QC 1763 were sieved through 400-mesh screen and the remaining samples were sieved through 270-mesh screen to remove large granules of metal powder. Samples QC 1762 through QC 1766 were dried simultaneously in a vacuum oven at 1.33 mPa and 200°C for 72 hr (Treatment II). During the drying procedure the off-gas was monitored by quadrupole mass spectrometry and was found to contain water only. Samples of J-4705-A were dried in separate experiments at 100° and 200°C for the drying efficiency study.

Samples QC 1762 through QC 1765 were subjected to 50% relative humidity for 48 hr (Treatment III). Sample QC 1766 ignited when exposed to air and could not be used in this study. The sample of J-4705-A dried at 200°C was divided into five equal parts and subjected to 50% relative humidity for the moisture absorption time study. The sample of J-4705-A dried at 100°C was subjected to 50% relative humidity for 48 hr (Treatment III). The three treatments reproduce conditions to which pyrotechnic materials may be subjected during production operations.

Triplicate one-gram samples of titanium metal powder from each treatment were sealed in 10-mm o.d. Pyrex glass tubes for NMR determination of total hydrogen content. Triplicate samples of J-4705-A were taken after 1, 8, 24, 48, and 72 hr exposure to 50% relative humidity. Samples from the air-dried treatment were submitted for surface area, oxygen, hydrogen, and emission spectroscopic analyses (Tables 1 and 2).

RESULTS AND DISCUSSION

The results of the moisture absorption study will be discussed in three parts. The first section will correlate the surface areas of titanium metal powder samples with moisture absorbed. The second section will discuss the absorption of moisture as a function of time in a sample of titanium metal powder of high-surface area. Finally, the effect of drying temperature on the moisture content of a sample of titanium metal powder of high-surface area will be presented.

Statistical tests [1,2] were performed on all the experimental results to evaluate the significance (at the 5% level) of any changes that occurred in the moisture content of the titanium metal powder samples due to drying technique (air-dried versus vacuum-dried), drying temperature (100°C versus 200°C), and moisture exposure time (0-144 hr). The overall precision (1σ = 0.0581 wt % moisture) of the experimental results was obtained by pooling [3] the sum of the squares of the differences between each observation and its mean for each treatment and each sample.

The purpose of drying the titanium metal powder in a high-vacuum furnace was to determine the actual amount of moisture absorbed by the material. To calculate the moisture from the difference in hydrogen content before and after drying is justified by the quadrupolar mass spectrometric analysis of the titanium metal powder off-gas during the heating process: only water was detected in the off-gas. High-vacuum drying is also necessary because pulsed NMR determines the total hydrogen content, comprised of OH^- and hydride hydrogen, of the samples. However, since the only component lost or gained in the drying and moisture exposure treatments is water, then the difference in total hydrogen content before and after each treatment should reveal the amount of moisture lost or gained. For convenience in presenting the data, all hydrogen results are given as weight percent moisture (Table 3).

Surface Area Study

The purpose of investigating the moisture absorption behavior of titanium metal powder as a function of surface area is the characterization of those material properties (both physical and chemical) which might influence the reliability of certain pyrotechnic devices. Also, since oxygen and hydrogen are omnipresent components of titanium metal powders, total oxygen (by neutron activation) and TiH_2 hydrogen (by PVT and mass spectrographic analyses of decomposed TiH_2) were determined for correlation with surface area. Titanium metal powders absorb moisture and oxygen from the atmosphere. Hydrogen is intentionally introduced into the synthesis of the powders.

Trace elemental analyses (Table 2) were also obtained for each titanium metal powder sample for future correlation with sample preparation (e.g., manner of synthesis and amount of surface area) and source of original material, and possibly with material performance in pyrotechnic devices or with other physical properties, such as resistivity measurement.

Plots of surface area as a function of moisture absorbed, hydride hydrogen (TiH_2), and total oxygen content are given in Figures 1-3. Excellent correlation (0.9799) is obtained with moisture absorbed, which indicates that the absorption occurs on the surface of the titanium metal powder particles. This is substantiated by the moisture absorption time study (Figure 4) which revealed that moisture equilibration in the titanium metal powder occurs very rapidly (~1 hr). If moisture diffused into the titanium particles, then a continuous increase in water should have been observed. No further increase in absorbed moisture was detected over the period (72 hr) of the experiment.

Although the moisture absorbed by titanium metal powder is directly related to the surface area, the amount of moisture (hydrogen other than TiH_2 or H_2O) retained in vac-dried samples is also a function of sample history (compare vac-dried J-4705-A with the QC series). Thus, there is a difference in the quality of titanium metal powders which can be measured by the hydrogen-retaining capacity. Total hydrogen retained by the vac-dried powder is a measure of sample quality, and net moisture absorbed is a measure of surface area. Sample quality is defined here as the uniformity in the chemical and physical properties of the titanium metal powders. Changes in the chemical and physical properties incurred by the titanium metal powder during manufacture and subsequent treatment can adversely affect quality and, hence, performance as a useful pyrotechnic material.

Other properties of titanium metal powders that can affect quality are hydride hydrogen (TiH_2) and total oxygen contents. Figures 2, 3, and 5 illustrate the relationships among the hydride hydrogen content, the total oxygen content, and the surface areas of two batches of titanium metal powders. Five samples of one batch (QC 1762 - QC 1766) and one sample of another batch (J-4705-A) were mechanically ground in water to achieve the range of surface areas listed in Table 1. It is obvious from Figures 2 and 3 that the relationship between oxygen or hydrogen and surface area is not linear. This is another indication that the quality levels of the titanium metal powder samples are not equivalent; specifically, the oxygen and hydrogen contents of sample J-4705-A differ markedly from the pattern established by the QC 1762 series of samples. As a function of surface area, both oxygen and hydrogen behave similarly (compare Figures 2 and 3). In fact, the oxygen and hydrogen contents of all the titanium metal powder samples correlate very well with one another (Figure 5). This correlation is probably fortuitous since the hydrogen is hydride hydrogen (TiH_2) and the oxygen is the total oxygen content of the samples. The hydrogen occurs in the ratio of four hydrogen atoms for every three oxygen atoms. No explanation is offered for this correlation, although it must be reconsidered if future studies repeat this finding.

Time Study

Since any factor which can alter the chemical or physical properties of titanium metal powders during manufacture and subsequent handling can adversely affect the reliability of pyrotechnic devices, it was part of this investigation to study the rate of moisture absorption by titanium metal powders. Figure 4 is a plot of the moisture absorption data given in Table 5 as a function of time-exposure in a 50% relative humidity atmosphere. Table 5 also includes base-line moisture data for air-dried samples of J-4705-A. Figure 4 dramatically illustrates that titanium metal powders absorb moisture rapidly, within an hour or less. Equilibration with atmospheric moisture is rapid and approaches the base-line figure of 0.64 wt %.

The initial drop in moisture content (minimum at 48 hr) could be due to formation of titanium hydride by the highly reactive titanium metal powders. Recall that these powders are high-surface area samples that were vacuum dried for 72 hr prior to exposure to moisture. The time study was not extended beyond 72 hr because it is believed that no additional moisture would be absorbed since the base-line value of 0.64 wt % moisture was obtained even for air-dried (40-60% relative humidity) material. The latter material had been stored for many months under water prior to the experimental treatments.

Drying Experiment

The effect of drying temperature on the moisture content of titanium metal powder sample J-4705-A was studied as an additional factor which might affect the reliability of pyrotechnic devices. Two temperatures were selected for the heat treatments: 100°C because it corresponds to the temperature used in the pyrotechnic program for drying titanium metal powders; and 200°C simply because a higher temperature might be more effective for drying. The results of the drying experiment are listed in Table 4 and demonstrate that for sample J-4705-A no significant difference was obtained between drying at 100°C and drying at 200°C. Thus, all the moisture that can be removed at 200°C in 72 hr essentially can be removed at 100°C in 72 hr.

CONCLUSIONS

Absorbed moisture, hydride hydrogen (TiH_2), and total oxygen in titanium metal powders are functions of surface area. Absorbed moisture is a linear function of surface area, probably because the moisture is absorbed only on the surface of the titanium metal powder particles. Hydride hydrogen and total oxygen contents are not linear functions of surface area. The hydrogen and oxygen are primarily introduced into the metal powder when it is mechanically ground in water to increase its surface area. Thus, the content of hydrogen and oxygen increases with surface because of the progressively increasing time of grinding.

Titanium metal powder sample J-4705-A was found to absorb an equilibrium quantity of moisture in one hour or less when exposed to a 50% relative humidity atmosphere. Comparison with the baseline moisture content of an air-dried sample indicated that the titanium metal powder sample had absorbed to capacity within an hour of exposure. Slight fluctuations in moisture content after the initial one-hour exposure period are attributed to reactions between moisture and the highly reactive metal powder to form hydrogen-containing species not recorded in our experiments.

It was found that drying titanium metal powder sample J-4705-A at 100°C is just as effective as drying at 200°C. Thus, it appears that the 100°C temperature presently used in drying the powder during the manufacture of pyrotechnic devices is sufficient to remove all the absorbed moisture.

The results of the pulsed NMR study of titanium metal powder indicate that pulsed NMR could be used as a rapid, nondestructive technique for monitoring the quality of this pyrotechnic material with regard to moisture and hydrogen content.

REFERENCES

1. A. Attalla, R. C. Bowman, Jr., B. D. Craft, C. M. Love, and R. L. Yauger, Investigation of Moisture in Titanium Metal Powder by Pulsed NMR, MLM-2418 (May 13, 1977), 9 pp.

2. J. C. R. Li, Statistical Inference I, Edwards Brothers, Inc., Ann Arbor, Michigan, Chapter 10, 1969.

3. Ibid, p. 144.

Table 1

ANALYTICAL DATA* FOR AIR-DRIED TITANIUM METAL POWDER SAMPLES

Mound QC Number	Sandia Mfg. Lot Number	Surface Area BET (m^2/g) Mound	Surface Area BET (m^2/g) Sandia	Hydrogen PVT (wt %)	Oxygen Neutron Activation (wt %)	Moisture 105°C, 1 hr (wt %)	Stoichiometry TiH_x (x)
1762 ET	II-DE-168-ZO	0.61	0.66	0.05	0.48	0.26	0.02
1763 ET	II-DE-168-ZA	3.35	2.53	0.17	2.31	0.50	0.08
1764 ET	II-DE-168-Z2A	5.72	4.35	0.35	4.34	0.57	0.17
1765 ET	II-DE-168-Z3A	7.59	5.38	0.55	6.75	0.66	0.26
1766 ET	II-DE-168-Z4A	8.05	6.45	0.71	9.50	0.41	0.34
**	J-4705-A	9.05	9.76	0.44	4.83	0.25	0.21

*The precision (1σ relative standard deviation) of the analytical data is ±1% for BET and PVT measurements, ±3% for neutron activation, and ±4% for moisture determinations.

**No Mound QC number has been assigned to this sample.

Table 2

TRACE IMPURITIES IN wt % AS DETERMINED IN AIR-DRIED TITANIUM METAL POWDER SAMPLES BY EMISSION SPECTROSCOPY

Sample	Copper Tin Boron	Ca	Si	Fe	Mn	Pb	Mg	Cr	Ga	Ni	Al	Zr
QC 1762	<0.005	0.2	0.1	0.08	0.04	<0.005	0.005	<0.005	<0.005	>0.2	>0.2	0.2
QC 1763	<0.005	0.2	0.2	0.08	0.05	<0.005	0.01	<0.005	<0.005	>0.2	>0.2	0.2
QC 1764	<0.005	0.2	0.2	0.08	0.04	<0.005	0.02	<0.005	<0.005	>0.2	>0.2	0.2
QC 1765	<0.005	0.2	0.2	0.08	0.05	<0.005	0.03	<0.005	<0.005	>0.2	>0.2	0.2
QC 1766	<0.005	0.2	0.2	0.08	0.05	<0.005	0.04	0.005	<0.005	>0.2	>0.2	0.2
J-4705-A	<0.005	0.05	0.03	0.08	0.005	0.009	>0.2	0.007	--	<0.005	0.1	0.05
QC 1779*	<0.005	--	0.15	0.1	--	--	0.3	<0.005	--	--	0.02	0.08

*Results for sample QC 1779 were discussed in an earlier report [1].

Table 3

MOISTURE IN wt %* AS DETERMINED BY PULSED NMR FOR TITANIUM METAL POWDERS SUBJECTED TO VARIOUS DRYING AND MOISTURE TREATMENTS

Sample	Treatment I (air-dried 16 days)	Treatment II (vac-furnace 72 hr)	Treatment III (vac-dried 50% relative humidity, 48 hr)	Treatments III,II (moisture absorbed)
QC 1762	0.28 ± 0.01	0.15 ± 0.01	0.23 ± 0.01	0.08 ± 0.02
QC 1763	0.71 ± 0.03	0.35 ± 0.02	0.50 ± 0.02	0.15 ± 0.04
QC 1764	0.84 ± 0.03	0.39 ± 0.01	0.71 ± 0.02	0.32 ± 0.03
QC 1765	1.04 ± 0.02	0.50 ± 0.02	0.84 ± 0.02	0.34 ± 0.04
QC 1766	1.06 ± 0.02	0.83 ± 0.04	**	**
J-4705-A	0.64 ± 0.02	0.15 ± 0.02	0.56 ± 0.01	0.41 ± 0.03

*Precision reported as ± 1σ absolute.

**Sample QC 1766 ignited when exposed to the atmosphere.

Table 4

MOISTURE DETERMINED FOR SAMPLE J-4705-A AT 50% RELATIVE HUMIDITY AFTER VACUUM DRYING AT 1.33 mPa AND 200°C

Moisture Exposure Time (hr)	Water (wt %)*
~380**	0.64 ± 0.02
0	0.15 ± 0.02
1	0.60 ± 0.01
8	0.60 ± 0.02
24	0.58 ± 0.01
48	0.56 ± 0.01
72	0.58 ± 0.01

*Precision reported as ±1σ absolute.

**This sample was air dried, not vacuum dried.

Table 5

MOISTURE CONTENT OF TITANIUM METAL POWDER SAMPLE J-4705-A AFTER DRYING AT 100°C AND 200°C

Sample Treatment	Water (wt %)*	
	100°C	200°C
Air-dried, 16 days	0.64 ± 0.02	0.64 ± 0.02
Vacuum dried, 72 hr	0.17 ± 0.01	0.15 ± 0.02
50% relative humidity, 48 hr	0.55 ± 0.01	0.56 ± 0.01

*Precision reported as ±1σ absolute.

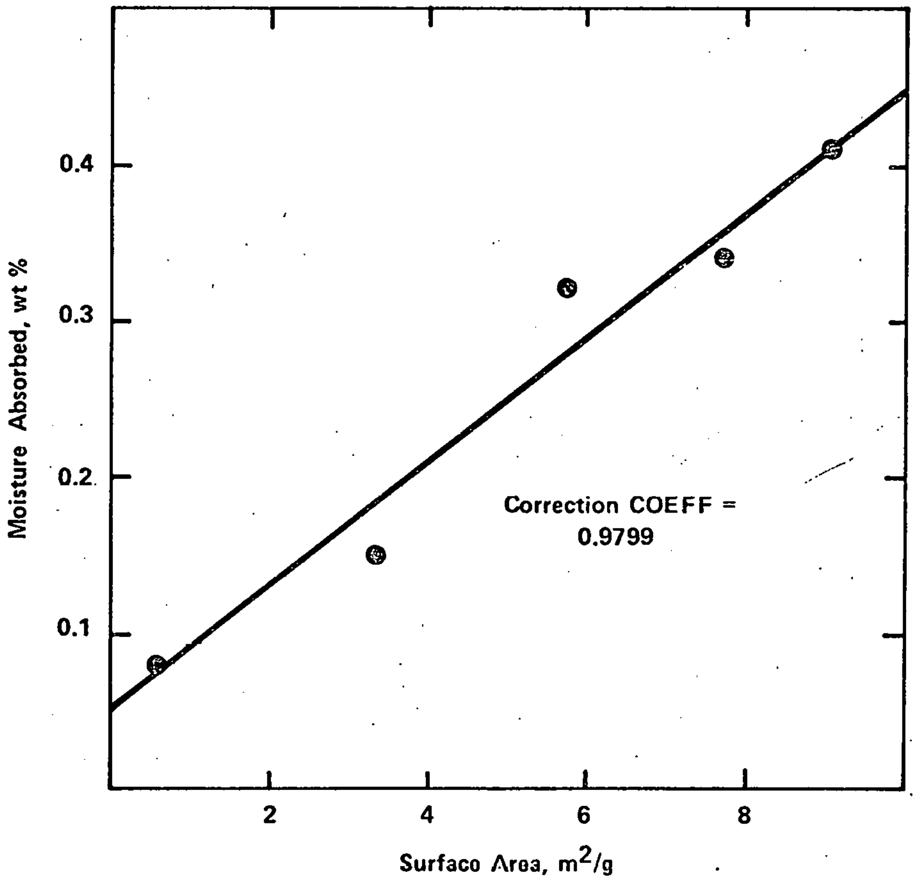

FIGURE 1 - Absorption of moisture increases with surface area in titanium metal powders.

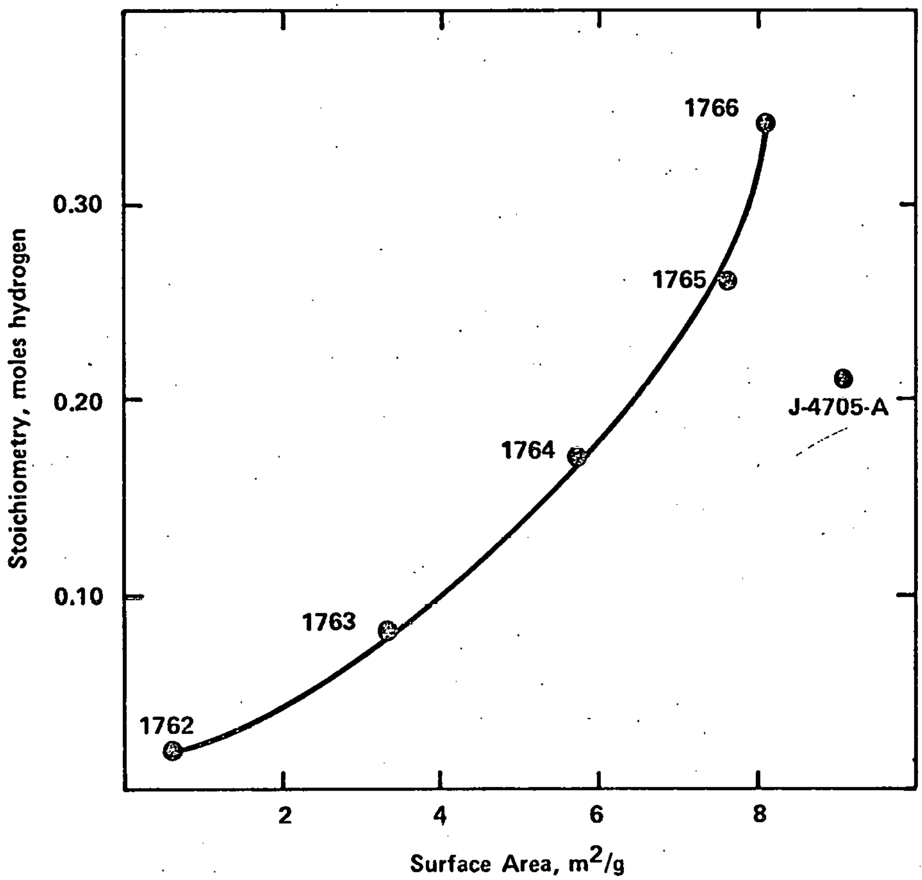

FIGURE 2 - Hydrogen content increases with surface area in air-dried samples of titanium metal powders.

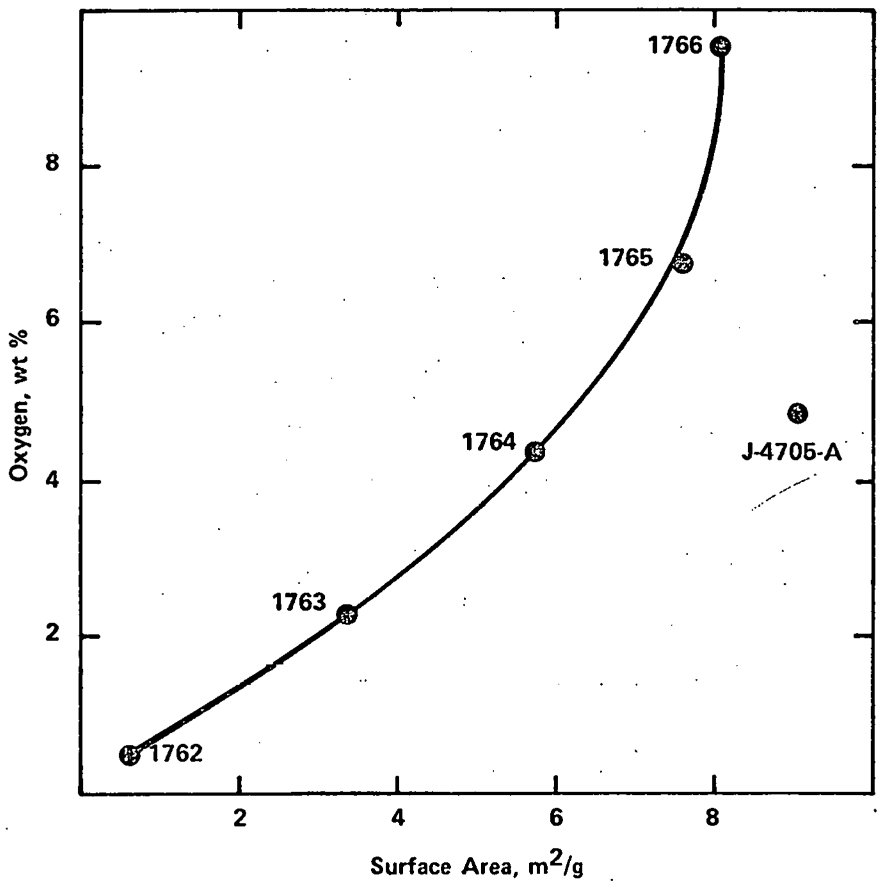

FIGURE 3 - Oxygen content increases with surface area in air-dried samples of titanium metal powders.

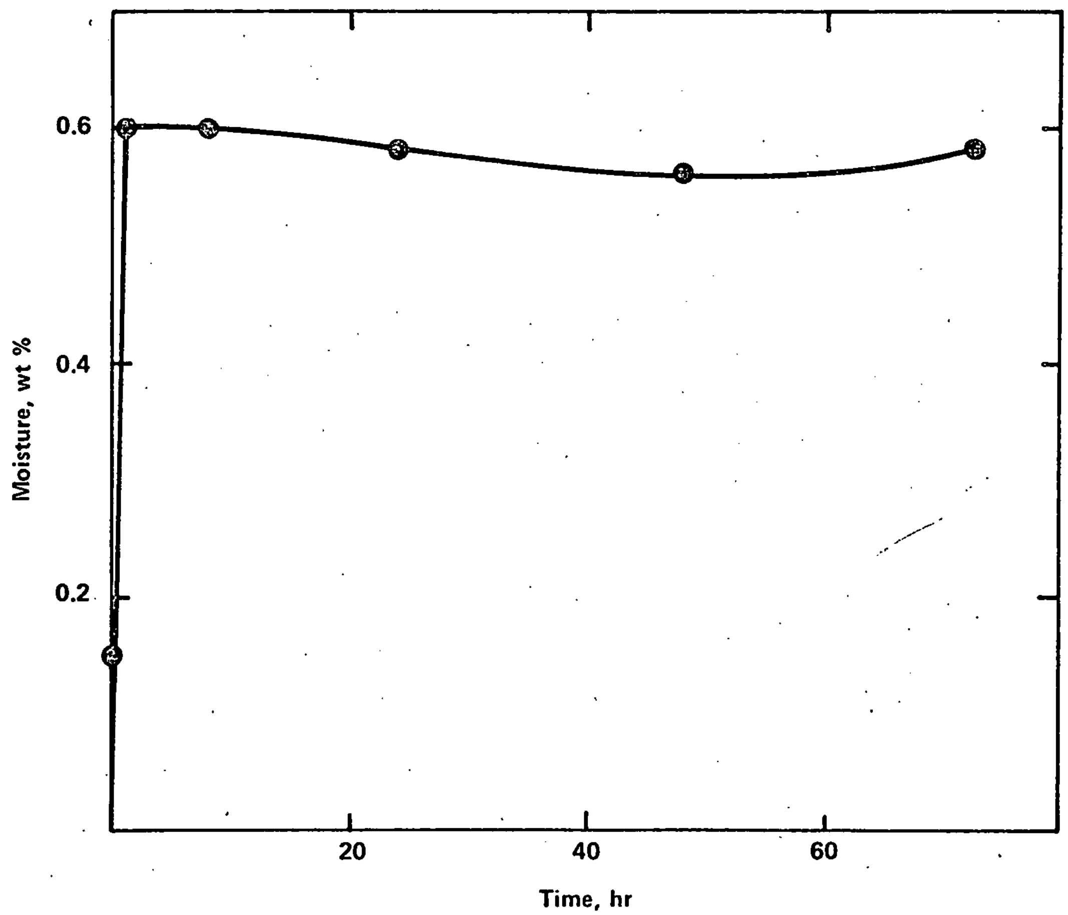

FIGURE 4 - Time study of moisture absorption in sample J-4705-A at 200°C, 1.33 mPa, and 50% relative humidity.

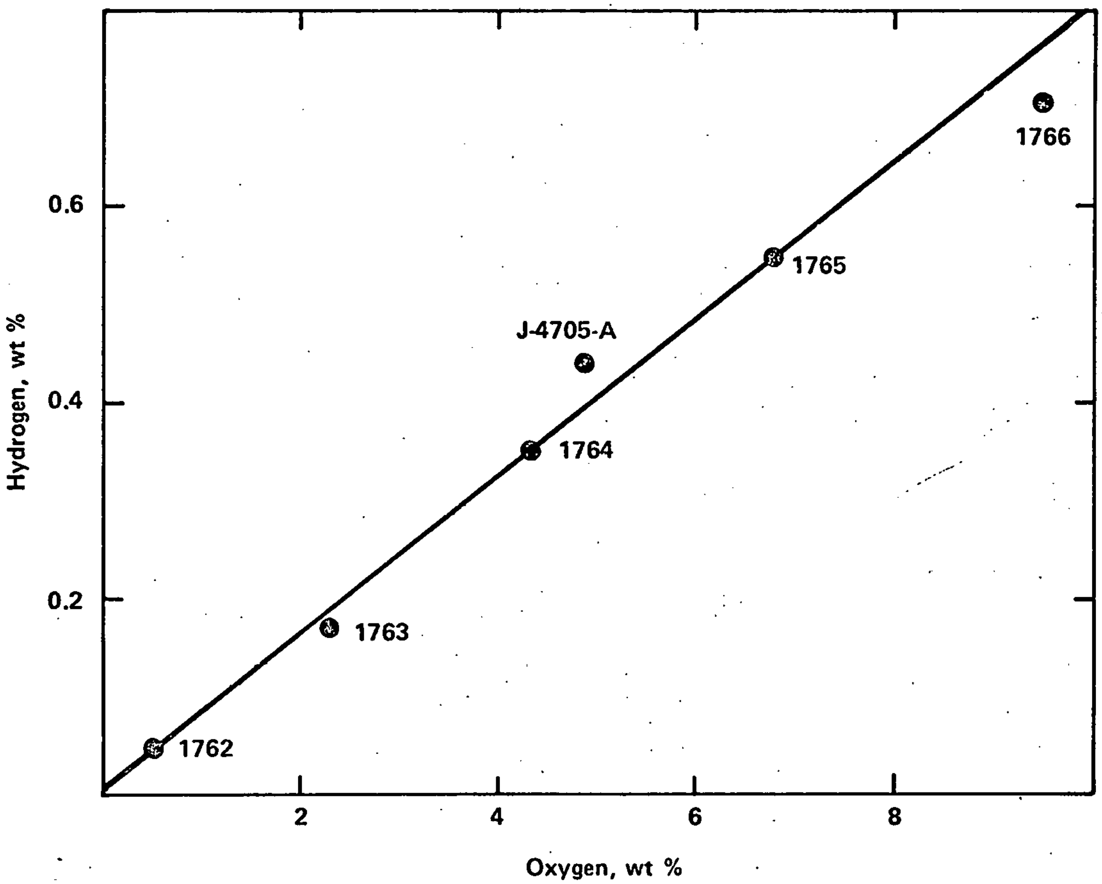

FIGURE 5 - Hydrogen content varies directly with oxygen content as surface area of titanium metal powders increases.