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Pyrotechnic Materials Development Program Review Meeting - January 18, 1977

Rod K. Quinn, Editor

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PYROTECHNIC MATERIALS DEVELOPMENT PROGRAM
REVIEW MEETING - JANUARY 18, 1977

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ABSTRACT

Current programs being conducted at Sandia Laboratories and Mound Laboratory in $Ti/KClO_4$ and $TiH_{0.65}/KClO_4$ pyrotechnic materials were reviewed. The subjects included chemical and mechanical properties of the starting materials and blends; e. g., electrical resistivity, chemical and mechanical analysis, and compatibility/stability studies; special problems associated with surface analysis of these materials; and results on mathematical modeling of ignition. After the presentations, a panel discussion was held. Suggestions for future actions in electrical and thermal conductivity, electrostatic pulse testing effects, ignition characteristics, pyrotechnic burn rate, compatibility, and communication of results were made.

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PYROTECHNIC MATERIALS DEVELOPMENT PROGRAM
REVIEW MEETING - JANUARY 18, 1977

Introduction

This is the first report on advanced development programs on pyrotechnic materials at Mound Laboratory and Sandia Laboratories. The report consists primarily of summaries of presentations at the first semiannual meeting and is divided into six sections corresponding to the general categories into which the programs fall. A conclusion summarizes the panel discussion and emphasizes subjects that require special attention.

The purpose of these meetings is to review individual and group technical programs in pyrotechnic materials, especially as they relate to pyrotechnic component development. The development programs range from basic materials synthesis and properties to compatibility and mechanical data on pyrotechnic blends.

Properties of the Starting Materials

Titanium Subhydride Fuel Synthesis (R. S. Carlson)

Titanium subhydride ($\text{TiH}_{0.65}$) fuel, manufactured in 150-g lots by Method V in a horizontal furnace and reactor, was developed through several stages of lot size and preparation method. The current Method V involves preparation from TiH_2 by removing gas at constant temperatures (438.5°C) for approximately 20 hours followed by cooling and passivating. A new horizontal rotating reactor capable of preparing a 1.5-kg batch is in design. Thus, the samples will be heated in a more precisely controlled furnace. Experiments in connection with the passivation step have shown that O_2 takeup per square meter is relatively constant from batch to batch and accounts for 10-20 percent of the total O_2 present in the subhydride. Composition vs. dehydriding temperature curves are related to the phase diagram, and a plot of final dynamic pressure at the end of the dehydriding step vs. composition at approximately 438.5°C can be used to halt accurately the process at any stoichiometry desired within closer tolerances than before. Van't Hoff plots of inverse temperature vs. log pressure for two samples of $\text{TiH}_{0.67-0.69}$ prepared from different starting materials and for $\text{TiH}_{0.68}$ and $\text{TiD}_{0.69}$ prepared from the same starting material show that there is no isotopic effect, verifying work by Haag and Shipko that the effect of differing impurity levels in the starting materials on the composition-pressure-temperature relationship is very important. Thermodynamic values for ΔH and ΔS are derived and are comparable to those of other workers. The plot also shows that the equilibrium pressure for $\text{TiH}_{0.68}$ at 350°C is 0.05 mm or less, and that hysteresis is not present. Viewgraphs for this talk are shown in Figs. 1-9.

The titanium metals being utilized in the pyrotechnic program are normally shipped and stored underwater. Although these materials undergo a drying procedure prior to blending with $KClO_4$, questions have arisen on the concentration of adsorbed water on the surface and the possible detrimental effects on the initiation process and stability of the pyrotechnic blend.

In the present study, various analytical methods are applied to evaluate the effectiveness of two specific drying procedures on moisture removal from high surface $TiH_{0.15}$ (QC-1779). The readsorption of water vapor was also investigated. Nuclear magnetic resonance (NMR) measurements lead to a determination of the adsorbed " H_2O " concentrations. The proton spin counts obtained by pulse NMR techniques have sufficient sensitivity to establish the following conclusions:

1. A significant amount of surface water is retained by high surface area Ti (i. e., ~1.2 weight percent for QC-1779 without drying at elevated temperature).
2. The conventional drying procedures are only partially effective in removing adsorbed H_2O .
3. Dried TiH_x will readsorb water from the air during room-temperature exposure where humidity is an important parameter.

Viewgraphs for this talk are shown in Figs. 10-17.

Oxidation Studies of Ti and TiH_x in Perchlorate Environment (R. K. Quinn)

In order to determine the role of oxide layers in compatibility, passivity, and spark sensitivity, we are examining the surface and interfacial chemistry of certain pyrotechnic materials. Initial experiments involved electrochemical oxidation of Ti thin films in $KClO_4$ solutions. The effects of the perchlorate medium on the oxidation of titanium metal are of interest, since these corrosive environments are extreme simulations of that potentially experienced by $Ti/KClO_4$ and $TiH_x/KClO_4$ blends as they are loaded into explosive components. Also very porous films with large surface-to-volume ratios are obtained by manipulating evaporation parameters. These films are analogous to powders in their surface properties. Current/voltage curves show the onset of current at $\sim +0.100$ V vs. saturated calomel electrode (SCE), and steady-state currents are achieved at $> +0.400$ V. This process is consistent with the initial dissolution of some fraction of the surface metal as Ti^{3+} and the subsequent oxidation to form oxides. Propagation of the oxide into the thin film proceeds as a linear function of applied voltage. Surface conductance measurements are possible on the Ti thin films because the film thickness (200-250 Å) approximates the inelastic mean free path (imfp) of the conduction electrons. Changes in surface composition are reflected in a change in conduction electron population and a subsequent change in surface conductance. With these films the absolute conductance drops as a function of applied voltage at a rate proportional to the rate of change of surface charge. Capacitance/potential data recorded simultaneously with a linear potential sweep experiment also indicated the irreversible

formation of surface oxide. From the electrochemical data we propose a model for oxide growth into the metal by ionic conduction from the metal/oxide interface to the oxide/solution interface and subsequent oxidation of the mobile species at that interface. Ionic conduction appears to be the field-dependent, rate-limiting process.

Both electrochemically treated and untreated Ti films were examined by Auger (AES) and X-ray photoelectron (ESCA) spectroscopy. Examination of the untreated and treated films indicated that the surfaces are not affected by electrochemical treatment, O/Ti $\approx$ 1.6-1.7 in all cases. The surface composition, as seen by ESCA, appears to be a combination of fully oxidized and fully reduced Ti with possible intermediate states. Sputtering removes the higher oxidation states of Ti leaving only Ti metal. The electrochemically oxidized films show oxide levels to greater depths, depending upon the extent of electrolytic treatment. The depth profiles were constructed by subtracting the depth profile for the blank film, and the resultant profiles are representative of the oxide produced electrochemically. The total excess oxide correlates well with the charge passed during oxidation. One further observation; no chlorine is observed in the sputtering profiles, further substantiating our model for oxide growth.

Future experiments will involve (a) oxidation studies in more corrosive environments; e. g., saturated KClO_4 , concentrated HClO_4 and HCl ; (b) oxidation of titanium hydrides; (c) solid/solid interaction studies; and (d) component hardware studies. Experiments are in progress to obtain comparative surface characterization of films, powders, and pressed pellets.

Viewgraphs for this talk are shown in Figs. 18-34.

Materials Properties of Ti/KClO_4 and $\text{TiH}_x/\text{KClO}_4$ Blends

Electrical Resistivity of TiH_x and $\text{TiH}_x/\text{KClO}_4$ Blends (J. W. Reed, J. E. Glaub)

The electrical resistivities of pressed pellets of TiH_x and $\text{TiH}_x/\text{KClO}_4$ blends were measured over a range of hydride stoichiometries and blend compositions. Measurements were carried out over a range of pressing loads from 5,000 to 20,000 psi. Attempts were made to measure the resistivity of pressed pellets by applying electrodes to opposite faces. The resistivity measurements by this technique were highly sensitive to contact pressure. A four-point probe technique for measuring resistivity appeared to solve the problem associated with contact resistance. The problem of repeatability or precision was not eliminated by this technique and appears to be characteristic of the pressed pellets. The precision of measurement at one point on the sample was good. When the position of the probe was changed, the measurement precision over the several positions became rather large. The precision was, however, sufficient to indicate trends and differences between blends, hydride composition and pressing densities. These differences in most cases were large compared to the measurement precision.

Viewgraphs for this talk are shown in Figs. 35-42.

X-Ray Diffraction Analyses of the $\text{TiH}_x/\text{KClO}_4$ System (D. B. Sullenger)

Debye-Scherrer powder X-ray diffraction analyses of $\text{TiH}_x/\text{KClO}_4$ materials have contributed substantially to pyrotechnic development and production via characterization of baseline Ti, TiH_x and KClO_4 ; assistance in finding a superior preparative method for TiH_x ; support of other teams in a variety of ways; and development of fundamental data for KClO_4 and for the Ti-H system. A brief résumé of the experimental technique employed, selection of standard patterns utilized and typical applications of the method during the Mound Pyrotechnic Project are presented. Planned future activities of diffraction analyses are indicated.

Viewgraphs for this talk are shown in Figs. 43-55.

Thermal Analyses of the $\text{TiH}_x/\text{KClO}_4$ System (J. W. Reed, J. L. Ivey, C. L. Fread, R. H. Steinmeyer, R. L. Yauger, G. C. Abell)

A combined experimental and theoretical study of the system $\text{TiH}_x/\text{KClO}_4$ was undertaken to investigate the thermodynamic and kinetic aspects of initiation of the $\text{TiH}_x/\text{KClO}_4$ pyrotechnic system and to obtain parameters of interest in mathematical modeling of the initiation and propagation from a hot bridgewire source. Experimental results along with kinetic computations will be of interest in understanding the chemical processes involved. Initial computations from a limited number of experimental reaction exotherms obtained by use of a differential scanning calorimeter have yielded a reasonably consistent set of kinetic parameters over a range of heating rates.

Viewgraphs for this talk are shown in Figs. 56-64.

Thermomechanical Analysis of $\text{TiH}_x/\text{KClO}_4$ Blends (T. M. Massis, P. K. Morenus)

A thermomechanical analysis (TMA) technique has been developed to simulate the decoupling or movement of the pyrotechnic away from the bridgewire in a loaded actuator configuration. By applying a force on the TMA probe assembly that rests against the pressed pyrotechnic in a loaded charge holder, the $\text{TiH}_{0.65}/\text{KClO}_4$ was observed to move or slip significantly in relation to the stationary charge holder material when thermally cycled from -50°C to $+150^\circ\text{C}$. A mismatch of greater than 2 to 1 in expansion coefficients of the $\text{TiH}_{0.65}/\text{KClO}_4$ and charge holder materials exists. This test setup simulated the forces applied to the actuator during component environmental testing that resulted in movement of the pyrotechnic material away from the bridgewire.

A design change to alleviate this problem through the use of a one-way washer or spring has been incorporated. This TMA technique has been used to prove the design change. Repeated thermal cycles using the one-way washer concept on the TMA have shown no movement of the pressed $\text{TiH}_{0.65}/\text{KClO}_4$ in relation to the charge holder; whereas without the washer pellet slippage was observed during the first cooling cycle.

Viewgraphs for this talk are shown in Figs. 65-76.

Compatibility Studies

Compatibility/Stability of $\text{TiH}_x/\text{KClO}_4$ Blends (T. M. Massis, P. K. Morenus, R. M. Merrill)

Compatibility and stability testing at Sandia Laboratories, Albuquerque, of the structural and pyrotechnic materials in the MC2949 and MC3004 has shown no incompatibility between the various materials in question or significant instability of the pyrotechnics Ti/KClO_4 or $\text{TiH}_{0.65}/\text{KClO}_4$. The chemical reactivity test (CRT), coupon stacks and loaded components are currently being aged to prove both compatibility and stability of the various materials in question. All these programs are continuing, with many of them planned to run for 3 years.

The extent of reaction or degree of instability of the Ti/KClO_4 and $\text{TiH}_{0.65}/\text{KClO}_4$ has been found to be some 4 to 10 times lower than that previously found for $\text{TiH}_{1.9}/\text{KClO}_4$ through the temperatures tested. For example, less than 0.3 percent of the Ti/KClO_4 and less than 0.15 percent of the $\text{TiH}_{0.65}/\text{KClO}_4$ have reacted through 300 days at 100°C in the CRT sample configuration. Under the same conditions, about 1-percent reactivity was measured for $\text{TiH}_{1.9}/\text{KClO}_4$.

Other observations include a surface area dependence on the amount of reactivity taking place (the greater the surface area of the fuel, the more reactive the material) and a greater reactivity in component geometry versus both the CRT and coupon configurations. Although a greater reactivity has been shown to exist for loaded components than for other testing techniques, compatibility or reliability has not been affected.

Viewgraphs for this talk are shown in Figs. 77-87.

Compatibility Program of Pyrotechnic Materials at Mound (L. W. Collins, G. E. Kettling)

An experiment was performed to determine if pyrotechnic powders adsorbed enough moisture during production handling to exceed the moisture specification. The analytical results from a 3-month exposure of Ti/KClO_4 and $\text{TiH}_{0.65}/\text{KClO}_4$ to controlled humidities showed that no statistically significant quantities of water were adsorbed by either sample. In another experiment, the catalytic effect of metal oxides on decomposition of potassium perchlorate was determined quantitatively. It was shown that extremely minute quantities of certain oxides significantly reduce the apparent decomposition temperature of KClO_4 --0.001 percent of Co_2O_3 lowered the decomposition temperature by more than 25°C . Isothermal weight loss measurements were used to compile a tabulation of the Arrhenius parameters for some common metal oxides with potassium perchlorate.

Current compatibility/stability studies at Mound Laboratory include chemical reactivity tests and chemiluminescence. Chemical reactivity tests for $\text{TiH}_{0.65}/\text{KClO}_4$ blends began in January and will extend through November. The feasibility of using chemiluminescence as an analytical tool for compatibility/stability studies is being investigated because of the unique advantages offered by this method.

Viewgraphs for this talk are shown in Figs. 88-101.

Additional Materials Studies

Compaction Studies of Pyrotechnic Blends (A. C. Munger)

An evaluation of compaction of pyrotechnic blends in charge holders was begun to investigate the variability in ETR data and firing times in various components.

It was discovered that the surface finish of the inner diameter of the charge holder greatly influenced the density achieved at the bridgewire. Force loss factors of up to 75 percent were discovered in some conditions.

The equipment was used to select loading parameters for various charge holder designs. Data obtained show that, although the force ratios are about the same for titanium and titanium subhydride blends, the final densities achieved at the same compaction forces are quite different.

Viewgraphs of this talk are shown in Figs. 102-109.

Surface Studies of Pyrotechnic Materials Used in Thermal Batteries (W. F. Swartz)

Three samples of iron powder, each of unique origin, have been characterized with respect to the segregation of impurities to the surface as a function of temperature. Data taken show that for the three specimens, sulfur segregation is essentially the same. However, the segregation of carbon in the temperature range from 25°-500°C is markedly different for each sample. It is very possible that the behavior of carbon could affect the performance of the various materials in pyrotechnic applications.

In an attempt to understand the carbon diffusion mechanism, the kinetics of the process were studied for Lot 24 and Lot 16. The activation energy of 6 kcal/mole for Lot 24 is consistent with a grain boundary diffusion phenomenon. Carbon diffusion in Lot 16 is markedly different, and the best estimate of an activation energy is approximately 24 kcal/mole, which is more consistent with a bulk diffusion process. Lot 16 has met specifications in thermal battery applications whereas Lot 24 has not with respect to burn rate.

Carbon in all lots thermally desorbs above 500°C in the form of gaseous carbon as determined by residual gas analyses (RGA) data.

With regard to sulfur segregation, Lots 11, 16 and 24 behave identically. Kinetic data taken on Lot 16 yield an activation energy of 17.6 kcal/mole, which is consistent with grain boundary diffusion in alpha-iron.

Since the sulfur behavior is essentially the same for all the iron powders studied, it is unlikely that the sulfur diffusion is the problem in pyrotechnic applications. It is felt that in these applications the carbon behavior is most critical.

Viewgraphs of this talk are shown in Figs 110-115.

Mathematical Modeling

Modeling of Pyrotechnic Ignition (A. B. Donaldson)

The hot-wire ignition conditions for a pyrotechnic are considered using a mathematical model. The model is based on the assumptions that the geometry is infinite in both the radial and axial directions, that the current passing through the bridgewire is constant, that all thermal and physical properties of both the bridgewire and pyrotechnic are constant, and that there is perfect thermal contact at the bridgewire-pyrotechnic interface.

The one-dimensional energy diffusion equation is employed to describe the pyrotechnic subject to bridgewire-pyrotechnic interface conditions that are specified by the current as well as by the system properties.

Based on either physical arguments or observation of analog or finite difference solutions, both the first and second spatial derivatives at the interface are found to change signs shortly before ignition. Hence, the occurrence of a null in these values is taken as the ignition criteria. By combining the remainder of the reactive diffusion equation with the interface conditions, an "ignition" temperature can be found. The time corresponding to the occurrence of this ignition temperature is then determined approximately from the inert (nonreactive) solution to the diffusion equation and interface conditions.

The results can then be matched to ignition data consisting of any two of the three variables ignition time, ignition temperature, or current level to deduce the reaction kinetics of the pyrotechnic. By this procedure, values for the preexponential factor have been estimated as 10^4 to 10^6 s^{-1} and the activation energy as 7 to 24 kcal/mole for $\text{TiH}_{1.9}/\text{KClO}_4$ (33/67).

Viewgraphs of this talk are shown in Figs. 116-122.

Summary of Panel Discussion

The summary section of this report contains a condensation of the panel discussion held at the end of the meeting. These items were taken from notes and a recording. The discussion has been organized into four different topical areas at the editor's discretion. Comments have been summarized, and suggested action has been indicated where appropriate.

Electrical and Thermal Conductivity of Pyrotechnic Materials

There was much discussion regarding the effects of parallel path resistance. It is not known whether changes in the measured bridgewire resistance (≤ 25 percent) are material or mechanical. These changes and their variabilities cause serious design problems. Two questions should be immediately addressed: (1) Does the material resistivity change after blending? (2) Is there an

experimentally significant variation in resistivity from sample lot to lot? These questions are being addressed at Mound by examining pellet conductivity as a function of several parameters.

Another key area of investigation is examination of the effect of oxide layers on the resistivity of powders. Currently, the effects of oxide layers on surface conductance of the metals and metal hydrides are being studied at Sandia. The effects of various oxide layer thicknesses on pyrotechnic properties will also be examined.

Another area in which studies are needed is that of possible physical and/or chemical changes in pressed blends as a function of testing, pressure, temperature, and time. Several possible techniques are being evaluated at Sandia by Divisions 2516 and 5822.

Electrostatic Pulse Testing and Its Effect on Unit Resistance

The measured bridgewire resistance in units can decrease by 15 percent upon testing with an electrostatic pulse (20 kV, 500 Ω , 600 pF). For the MC2949 actuator this pulse is a field requirement and therefore must be addressed. To bring units back to the specified bridgewire resistance, thermal cycling is required. Component tests are being conducted by A. C. Munger, Mound, on 75 units to look at this effect and its magnitude. The suggestion was made to reconvene at least part of the attendees and present these data when available. B. R. Steele of SLA made the point that this resistance decrease has been observed for the MC2949 and the MC3004--two different configurations and two different materials ($\text{TiH}_{0.65}/\text{KClO}_4$ and Ti/KClO_4).

Ignition Characteristics

Another area that was considered was that of ignition sensitivity. Although this is a key property for actuator function, little work has been done. No specific suggestions were made. However, subsequent conversations have indicated the possible use of laser-induced and minislapper ignition techniques.

Burn Rate Studies

Some attention in the overall advanced development program should be given to burn rate. It was concluded that an experimental gap exists, and that techniques existing throughout the weapons laboratory system should be considered for this program. Two experimental apparatuses at Mound were mentioned--J. Mohler's optical technique for measuring the burn front and C. Chong's apparatus for looking at reaction rate by mass spectrometrically examining products and measuring pressure and temperature excursions. Ray Ng of SLL also mentioned his experiments to measure pressure-time into zero volume. He has in addition looked at velocity as a function of time with a VISAR. The laser technique used at UMC for heat pellets was mentioned.

The major conclusion in this area is that development of a burn rate or reaction rate measuring capability at Mound should be a priority since data is required on actuators during and after firing.

Compatibility

Two design engineers who are working on components using these pyrotechnic materials (A. K. Jacobson and B. R. Steele) expressed concern over the 24-year life requirement and materials compatibility. After considerable discussion, it was decided that through the work being done by T. M. Massis at SLA and Mound, much of this area was being covered. Subsequent to the meeting, a counterpart to Massis was named at Mound. L. W. Collins will coordinate Mound's compatibility studies, and the whole effort between the two laboratories will be coordinated through T. M. Massis.

The problem of what tests could be conducted to define an acceptable humidity range in the blending and loading areas was discussed. The electrical conductivity and NMR techniques were suggested as possibilities.

Communication

The final major area of discussion was that of communication of information between the individual staff members at the two laboratories. Two mechanisms were proposed. Review meetings will be held twice a year on an alternating basis between Mound Laboratory and Sandia Laboratories to discuss individual advanced development programs and exchange ideas on which programs should be implemented, altered and/or continued. The minutes and discussion contained in this report indicate this criterion was met for the first meeting. The second mechanism of information exchange should be a short (less than one page) written description of each individual's timely contributions to specified program areas. These short reports should be made at least quarterly in an informal format, possibly in the component status reports. Details are being worked out at this time.

The author apologizes to those individuals whose comments and/or suggestions may have been omitted. P. G. Neiswander and L. Cafferty are gratefully acknowledged for their help in compiling these minutes.

FIGS. 1-9 - VIEWGRAPHS FROM PRESENTATION BY R. S. CARLSON

Fig. 1 - Oxygen Absorption vs. Bet Surface Area of Titanium Subhydrides

Batch QC Number	H/Ti Ratio	Air Fraction f^a	Air Absorbed (n_A/m^2 $\times 10^5$) ^b	QC of Starting Material	Air Absorbed (wt %)	Air Absorbed Total O ₂ Content of Subhydride (wt %)
1711	0.64	0.239	5.51	1709		
1713/1714	0.70 (av)	0.205	5.97	1709		
1718/1719	0.64 (av)	0.189	4.60	1709		
1724/1725	0.55 (av)	0.209	5.78	1709		
1730/1731	0.64 (av)	0.226	4.57	1709		
1732/1733	0.64 (av)	0.209	5.71	1709		
1739/1740	0.36 (av)	0.243	7.37	1709		
1741/1742	0.04 (av)	0.218	6.64	1623		
1743	1.44	0.235	6.11	1709	0.263	15.4
1744	1.52	0.234	5.47	1709	0.263	15.4
1747	1.47	0.292	4.97	1709 ^c	1.16	18.5
1749	1.11	0.259	8.09	1709	0.261	15.1
1761	0.63	0.238	8.58	1747 ^d	1.64	18.4
1782/1783	0.67 (av)	0.249	5.53	1709	0.176	10.6
1784/1785	0.66 (av)			1623		
1791P	0.67		5.66	1709	0.182	10.2
1792P	0.67	0.235	5.38	1709	0.174	10.3

NOTES:

^a
 f = fraction of air admitted to reactor which is absorbed by titanium subhydride.

$$f = \frac{nP_I - (P_{f1} + P_{f2} + \dots + P_{fn})}{nP_I}$$

where n = number of gas additions

P_I = initial pressure in chamber before absorption

P_f = final pressure in chamber after absorption

^b
 n_A = moles air absorbed

m^2 = total surface area of subhydride in m^2 .

^cBallmilled QC1709. BET S. A. = $7.84 m^2/g$.

^dBallmilled QC1747. BET S. A. = $6.35 m^2/g$.

Fig. 2 - Composition vs. Dehydrating Temperature at 20 hr.

Fig. 3 - Phase Diagram for Ti-H System

Fig. 4 - Final Dynamic Pressure vs. Composition

Fig. 5 -

Fig. 6 - Analytical Results (Wt. %) - Type 6

	QC-1709A	QC-1779	QC-1792P
O ₂	1.5	5.19	1.69
N ₂	0.3	0.4	
Fe	0.015	0.1	0.01
Na	440 PPM (AA)	-	230 PPM
Mg	< 0.003	≥ 0.3	< 0.005
Si	0.005	0.15	0.01
Al	0.03	0.02	0.04
Ni	< 0.003	< 0.005	< 0.005
Cu	< 0.003	0.007	
Zr	0.01	0.08	0.01
Cr	0.003	≤ 0.005	< 0.005

Fig. 7 - Thermodynamic Properties

Calculations $\log P_{\text{atm}} = \frac{-A}{T} + B$ $A = \frac{\Delta H}{2.303} (1.987)$

TiH_{0.67} QC-1792P (QC-1709A) $B = \frac{-\Delta S}{2.303} (1.987)$
40 at. % hydrogen, β region

$A = -6711.4$ $\Delta H = -30.71 \text{ Kcal/mole}$ Temp. Range
 $B = 9.53$ $\Delta S = -29.88 \text{ cal/}^\circ\text{K/mole}$ 439.8-487.0°C

$A = -7843.14$ $\Delta H = -35.89 \text{ Kcal/mole}$
 $B = 8.05$ $\Delta S = -36.84 \text{ cal/}^\circ\text{K/mole}$ 359.2-387.5°C

TiK_{0.69} (QC-1779)

$A = -7168.46$ $\Delta H = -32.80 \text{ Kcal/mole}$ 345-450°C
 $B = 7.33$ $\Delta S = -33.6 \text{ cal/}^\circ\text{K/mole}$

TiD_{0.68} (QC-1779)

$A = -7299.3$ $\Delta H = -33.4 \text{ Kcal/mole}$
 $B = 7.57$ $\Delta S = -34.63 \text{ cal/}^\circ\text{K/mole}$ 402-486°C

Haag & Shipko
Ti-H system JACS 78:5155 (1956)

$\Delta H_{\text{sol}} = 32.4 \text{ Kcal/mole of}$
 $\text{H}_2 \text{ @ 20 at.}$
 $\% \text{ @ 450}^\circ\text{C}$
 $(\text{TiH}_{0.25})$
 $(\alpha + \beta \text{ phase})$

Fig. 8 - Titanium Subhydride Batches Produced in Vertical Tube Reactor

Batch	QC No.	Weight (g)	H/Ti	Starting Material QC	Method*	Comments
1633	-	65.3	0.50	1621	I	Titanium contaminated - 0.3 mCi/g TiH _{0.5}
1634	-	68.1	0.83	1621	I	
1635	-	67.1	1.08	1621	I	
1636	-	69.1	1.35	1621	I	
1637	-	64.3	1.55	1621	II	
1643	-	37.2	1.37 (est)	1621	II	
1644	-	48.5	1.61	1621	II	
1649	-	38.5	1.73	1621	II	
1650	-	43.3	1.91	1621	II	
1651	-	54.7	1.81	1621	II	
1652	-	39.4	1.97	1621	II	
1660	-	38.5	1.59	1621	III	
1663	-	52.5	1.73	1623	IIIA	
1664	-	52.5	1.52	1623	IIIA	
1665	-	53.5	1.73	1623	IV	
1666	-	50.6	1.47	1623	IV	
1667	-	53.9	1.21	1623	IV	
1668	-	59.3	0.89	1623	IV	
1669	-	56.9	1.60	1623	V	
1670	-	45.0	0.09	1623	V	Sintered to a hard cylinder
1674	-	25.8	0.56	1623	V	
1676	-	23.2	0.91	1623	V	
1677	-	26.6	0.68	1623	V	
1678	-	25.6	0.57	1623	V	
1679	-	25.3	0.51	1623	V	
1680	-	26.0	0.18	1623	V	
1681	-	27.1	0.60	1623	V	
1682	-	27.6	0.74	1623	V	
1683	-	80.9	0.59	1623	V	Blended from QC-1674, 1678, 1679, 1681, and 1677.
1687	-	28.7	0.56	1623	V	
1690	-	25.1	0.61	1623	V	
1691	-	29.6	0.62	1623	V	
1692	-	24.8	1.13	1623	V	
1693	-	26.3	0.62	1623	V	
1694	-	25.5	0.79	1623	V	
1695	-	26.2	0.70	1623	V	
1698	-	25.8	0.74	1623	V	
1699	-	26.2	0.76	1623	V	
1700	-	25.8	0.94	1623	V	
1701	-	24.9	0.68	1623	V	
1705	-	25.9	0.75	1623	V	

Total 42 batches

Fig. 9 - Titanium Subhydride Batches Produced in 2-1/2 In. O. D. Horizontal Tube Reactor

Batch QC No.	Weight (g)	H/Ti	Starting Material QC	Method	Comments
1702	15.0	0.03	1623	V	
1703	15.0	0.62	1623	V	
1704	15.0	1.03	1623	V	
1706	150.0	1.20	1623	V	
1707	150.0	1.04	1623	V	
1708	150.0	0.35	1623	V	
1710	150.0	0.83	1709	V	This material was extensively analyzed to determine composition (and temp.) profile in tray. Both SLA and Mound did O ₂ , BET, H/Ti and emission spectroscopy on 7 discrete samples from this batch (one tray configuration). Sampled at 13 points. Two tray configuration with material in left hand 8-10" of tray. Set standard for all future batches.
1711	150.0	0.64	1709	V	
1712	150.0	0.75	1709	V	
1713	80.0	0.72	1709	V	One synthesis. Each tray received a separate QC number.
1714	70.0	0.68	1709	V	
1718	80.0	0.65	1709	V	
1719	70.0	0.64	1709	V	
1720	80.0	0.49	1709	V	
1721	70.0	0.45	1709	V	
1722	80.0	0.35	1709	V	
1723	70.0	0.31	1709	V	
1724	80.0	0.57	1709	V	
1725	70.0	0.54	1709	V	
1726	80.0	0.69	1709	V	
1727	70.0	0.66	1709	V	
1728	80.0	0.64	1709	V	
1729	70.0	0.61	1709	V	
1730	80.0	0.65	1709	V	
1731	70.0	0.63	1709	V	
1732	80.0	0.65	1709	V	
1733	70.0	0.62	1709	V	
1739	80.0	0.38	1709	V	
1740	70.0	0.33	1709	V	
1741	80.0	0.65	1709	V	
1742	70.0	0.63	1709	V	
1743	80.0	1.45	1709	V	80.0 g in bottom tray.
1744	80.0	1.52	1709	V	
1745	80.0	1.60	1709	V	
1746	80.0	1.90	1709	V	
1747	64.0	1.47	Ballmilled 1709	V	In bottom tray.
1748	80.0	1.32	1709	V	
1749	80.0	1.11	1709	V	
1761	30.2	0.63	(If corrected for Q ₂ = 0.69) 1747	V	High surface area fraction of QC 1747
1781	68.8	This material was QC1623 fractionated into 5 fractions. See Ref. 2.			
1782	80.0	0.68	1709	V	
1783	70.0	0.65	1709	V	
1784	80.0	0.67	1709	V	One synthesis. Each tray received a separate QC number.
1785	80.0	0.64	1709	V	
1790-P	150.0	0.68	1709A	V	QC1709 thoroughly blended and repacked and called QC1709A. This is first production batch (indicated by -P).
1791-P	150.0	0.67	1709A	V	
1792-P	150.0	0.67	1709A	V	
1793-P	150.0	0.64	1709A	V	
1794-P	150.0	0.63	1709A	V	5 Spot samples within 0.03 H/Ti of specification.
None	25.0 g powder & 2.5 g of metal		1779 & Ti metal slices	I	Material deuterided to 0.68 (powder) and 0.91 (sheet).
None	25.0 g powder		1779	I	Material hydrided to 0.69.

49 Batches to 9-15-76

FIGS. 10-17 - VIEWGRAPHS FROM PRESENTATION BY R. C. BOWMAN

Fig. 10 - Characterization of Adsorbed H_2O On High Surface Area Titanium

I. Objectives:

- Determine Concentration of Adsorbed H_2O
- Evaluate Effectiveness of Drying Procedures
- Determine Readsorption of H_2O After Drying

II. Primary Interest is High Surface Area Ti "Metal" - Shipped and Stored Under Water

Fig. 11 - Normal Components in Ti - "Metal"

- α - Phase Ti Metal
- γ - Phase $\text{TiH} \approx 1.5$
- TiO_2 (Surface Film of $\approx 20\text{-}30 \text{ \AA}$)
- Adsorbed H_2O and OH species
- Miscellaneous Impurities

Fig. 12 - NMR Spin Counting Techniques

I. Free Induction Decay (FID) - Pulse NMR

A. Decay Time Sensitive to Local Structure

- Short ($\leq 10 \mu\text{s}$) - Rigid Atom in Bulk
- Long ($\geq 50 \mu\text{s}$) - Mobile Species (surface)

B. Initial FID Amplitude - Concentration

II. Typical FID for $\text{TiH}_{0.15}$ (QC-1779)

Fig. 13 - Sample Properties and Analytical Data QC-1779
(Ventron Lot #II-RS-14)

Nominal Stoichiometry: $\text{TiH}_{0.15}$
 Surface Area: $4.06 \text{ M}^2/\text{G}$
 Moisture (CEC Analyzer): 0.42 weight/percent

<u>Elemental Analyses</u>	<u>Weight/Percent</u>
Ti	94.48
O	5.19 ± 0.11
H	0.31
N	0.4 ± 0.2
Mg	≥ 0.3
Si	0.15
C	0.10

Fig. 14 - Experimental Treatments

	<u>Treatment</u>	<u>Pressure (torr)</u>	<u>Temperature (°C)</u>	<u>Time (hr)</u>	<u>Sample Handling</u>
I.	Air-Dried	Ambient	R. T.	> 72	Air
II.	High-Vac.	$\sim 10^{-5}$	190-5	88	Inert & Vac.
III.	Vac. Furnace	5×10^{-2}	105	24	Inert & Vac.
IV.	III + Air	-	R. T.	1	Air
V.	IV + 100% Rel. Humidity	-	R. T.	45	Air

Fig. 15 - Results for QC-1779

NMR-Concentration (weight/percent)

<u>Sample</u>	<u>Treatment</u>	<u>"H" (Mot. Nar.)*</u>	<u>"H₂O"</u>
I	Air-Dried	0.129 ± 0.003	1.16 ± 0.02
II	High Vacuum-Inert	0.051 ± 0.005	0.46 ± 0.05
III	Vacuum-Inert	0.083 ± 0.006	0.75 ± 0.05
IV	Vacuum-1 hr Air	0.099 ± 0.006	0.89 ± 0.05
V	Vacuum-45 hr 100% Relative Humidity	0.172 ± 0.016	1.55 ± 0.14

* Motionally narrowed; refer to Fig. 12, Mobile "H".

Fig. 16 - Summary

- I. QC-1779 Assuming Only H_2O for Proton FID
 - A. Normal Drying Procedures Only Partially Effective
 - CEC Moisture Analysis Represents Differences.
 - Removes Weakly Bound H_2O and OH Species.
 - B. Readily Readsorbs H_2O From Water Vapor.
 - C. These Findings Probably Valid for All TiH_x

Fig. 17 - Comparison With Infrared Studies of TiO_2 Surfaces

- A. Several Forms for Adsorbed H_2O and OH Species.
 - Chemisorption - Various OH
 - Strong Molecular Adsorption
 - Weak Molecular Adsorption
- B. H_2O Removal Incomplete Below 300°C
- C. Reversible Reactions With Water Vapor at Room Temperature

FIGS. 18-34 - VIEWGRAPHS FROM PRESENTATION BY R. K. QUINN

Fig. 18 - Interfacial Electrochemistry

PAR 173 Potentiostat with auxiliary equipment permits measure of:

- (a) Current - voltage
- (b) Charge - voltage
- (c) Capacitance
- (d) Surface conductance*

Thin Film Electrodes:

200-600 Å Ti

deposited at 25 C to 500 C

on SiO_2 or Al_2O_3 substrates

SURFACE ANALYSIS

AES/ESCA - PHI-548 Spectrometer

Fig. 19 - Current (i), charge (Q) and surface resistance (ΔR) as a function of applied potential for a 200 Å Ti electrode in 1N KClO_4

Fig. 20 - AES spectrum of Ti blank surface

Fig. 21 - $dN(E)/dE$ and $N(E)$ for Ti (LMM) AES peaks. Note structure of $N(E)$ for high-energy Ti peak.

Fig. 22 - AES spectrum of Ti blank surface in Fig. 20 after 6 minutes of argon ion etching.

Fig. 23 - AES spectrum of Ti blank surface of Fig. 22 with $N(E)$ of Ti(LMM) peaks. Compare $N(E)$ of high energy peak to that of Fig. 21.

Fig. 24 - Table of ESCA peaks for several Ti thin film electrodes.
The ΔBE terms are defined at bottom of figure.

	TiO ₂ STANDARD (PRESSED PELLET)	Ti BLANK (SLIGHTLY SPUTTERED)	Ti BLANK (WELL SPUTTERED)	TiO ₂ POLYCRYSTALLINE FILM (REDUCED)
Ti (2p _{3/2})	461.7 eV	460.0 eV	456.0 eV	460.4 eV
O (1s)	533.2 eV	531.7 eV	≈ 533 eV	531.9 eV
$\Delta BE_{(1)}$	71.5 eV	71.7 eV	77.0 eV	71.0 eV
Ti(A)	870.0 eV	874.5 eV	870.0 eV	875.5 eV
$\Delta BE_{(2)}$	408.3 eV	414.5 eV	417.0 eV	415.1 eV

$$\Delta BE_{(1)} = O(1s) - Ti(2p_{3/2})$$

$$\Delta BE_{(2)} = Ti(AUGER) - Ti(2p_{3/2})$$

Fig. 25 - ESCA spectrum of Ti blank film. The principal peak is the Ti(2p_{3/2}) with a higher energy shoulder for Ti (2p_{1/2}).

Fig. 26 - ESCA spectrum of Ti ($2p_{3/2}$ & $2p_{1/2}$) peaks for a TiO_2 standard.

Fig. 27 - AES spectrum of Ti thin-film electrode after 4mC of oxidative change. Note similarity to Ti blank in Fig. 20.

Fig. 28 - $dN(E)/dE$ and $N(E)$ as a function E for the electrode of Fig. 27. Compare this spectrum to that of Fig. 21

Fig. 29 - $dN(E)/dE$ and $N(E)$ as a function of E for the electrode of Figs. 27 and 28 after 3 minutes of ion etching. Note $N(E)$ spectrum is similar to that of the blank shown in Fig. 23.

Fig. 30 - Corrected depth profile of oxygen to titanium for a blank Ti film electrode.

Fig. 31 - Corrected depth profile of Ti film electrode after 4mC of oxidative change. Normalized curve is that obtained after corrections for the blank profile (Fig. 30),

Fig. 32 - Corrected depth profile for Ti thin film electrode after 13 mC of oxidative change.

Fig. 33 - Correlation of relative excess oxide thickness from the normalized profile to the amount of oxidative change passed.

Fig. 34 - Proposed Future Work in this Area

(a) Increase Corrosive Environment

- Saturated KClO_4
- Concentrated HClO_4
- Concentrated HCl

(b) Titanium Hydrides

(c) Solid/Solid Interaction

(d) Other Component Hardware Parts

e.g. Kovar, Nichrome

(e) Comparative Surface Characterization of

- Powders
- Pellets
- Films

FIGS. 35-42 - VIEWGRAPHS FROM PRESENTATION BY J. W. REED

Fig. 35 - Resistivity as a Function of TiH_x Stoichiometry

Composition QC No.	10 Kpsi Pressing Load			
	Top Surface		Bottom Surface	
	$\rho(\Omega\text{-cm})$	% Dev.	$\rho(\Omega\text{-cm})$	% Dev.
$\text{TiH}_{1.9}$	14.38	34	11.9	47
QC-1623	12.4	24		
$\text{TiH}_{1.47}$	10.8	9	6.70	7
QC-1747	7.5	35	5.0	24
$\text{TiH}_{0.78}$	0.245	5	0.191	13
QC-1726B (2.49 m^2/g)				
$\text{TiH}_{0.65}$			0.013	6
QC-1787				
$\text{TiH}_{0.3}$	0.059	11	0.130	36
QC-1675	0.063	13	0.074	12
$\text{TiH}_{0.2}$				
QC-1767				

Fig. 36 - Resistivity as a Function of TiH_x Stoichiometry

Composition QC No.	30 Kpsi Pressing Load			
	Top Surface		Bottom Surface	
	$\rho(\Omega\text{-cm})$	% Dev.	$\rho(\Omega\text{-cm})$	% Dev.
$\text{TiH}_{1.9}$	2.09	12	3.02	24
QC-1623	1.75	12	4.67	24
$\text{TiH}_{1.47}$	0.44	24	0.68	11
QC-1747				
$\text{TiH}_{0.78}$	0.066	8	0.066	2
QC-1726B (2.49 m^2/g)				
$\text{TiH}_{0.65}$	0.007	36	0.028	33
QC-1787				
$\text{TiH}_{0.2}$	0.036	5	0.029	3
QC-1675				
$\text{TiH}_{0.2}$	0.262	7	0.256	14
QC-1767				

Fig. 37 - Resistivity of TiH_x as a Function of Hydride Stoichiometry

Fig. 38 - Resistivity of Several $\text{TiH}_x\text{KClO}_4$ Blends

PO-3088		PO-3089		PO-3087		PO-2040	
$\text{TiH}_{0.65}/\text{KClO}_4$		$\text{TiH}_{0.65}/\text{KClO}_4$		$\text{TiH}_{1.1}/\text{KClO}_4$		$\text{TiH}_{0.2}/\text{KClO}_4$	
10 kpsi	20 kpsi	10 kpsi	20 kpsi	10 kpsi	20 kpsi	10 kpsi	20 kpsi
Ω-cm	Ω-cm	Ω-cm	Ω-cm	Ω-cm	Ω-cm	Ω-cm	Ω-cm
472	1.21	28.2	0.88	1172	4.31	3.08	0.44
150	1.43	30.6	0.96	-	7.36	3.75	0.51

Fig. 39 - Resistivity of Pressed Pellets of Sample
QC-1823P ($\text{TiH}_{0.65}$) as a Function of Time

Elapsed Time (Days)	10 kpsi Load				20 kpsi Load			
	FACE 1		FACE 2		FACE 1		FACE 2	
	$\rho(\Omega\text{-cm})$	% Dev	$\rho(\Omega\text{-cm})$	% Dev	$\rho(\Omega\text{-cm})$	% Dev	$\rho(\Omega\text{-cm})$	% Dev
0.02	0.00392	6.7	0.00356	5.8	0.00175	2.6	0.00179	1.4
0.75	0.00358	6.7	0.00326	0.6				
3	0.00347	6.7	0.00358	3.7				
7	0.00371	8	0.00367	2.3	0.00186	3.4	0.00180	1

Fig. 40 - Resistivity of $\text{TiH}_{0.65}$ From Time of Preparation

Fig. 41 - Resistivity of Sample PO-3086 With Pressure

5 kpsi		10 kpsi		20 kpsi	
Resistivity (Ω/cm)	Std. Dev. %	Resistivity (Ω/cm)	Std. Dev. %	Resistivity (Ω/cm)	Std. Dev. %
58	43	2.1	22	0.44	.9
511	111	2.0	15	0.53	0.7
103	42	2.53	1.2	0.46	6.0
103	19	4.30	0.3	0.55	0.2

Fig. 42 -

FIGS. 43-55 - VIEWGRAPHS FROM PRESENTATION BY D. B. SULLENGER

Fig. 43 -

DEBYE-SCHERRER POWDER X-RAY DIFFRACTION ANALYSES
OF TiH_x - KClO_4 MATERIALS HAVE CONTRIBUTED SUBSTANTIALLY
TO PYROTECHNIC DEVELOPMENT AND PRODUCTION VIA:

1. CHARACTERIZING BASELINE Ti , TiH_x AND KClO_4 ;
2. ASSISTING IN FINDING A SUPERIOR PREPARATIVE METHOD
FOR TiH_x ;
3. SUPPORTING OTHER TEAMS IN A VARIETY OF WAYS;
4. DEVELOPING FUNDAMENTAL DATA FOR KClO_4 AND
FOR THE Ti-H SYSTEM

AS THE PROJECT CONTINUES POWDER X-RAY DIFFRACTION WILL REMAIN A
KEY METHOD OF ANALYSIS.

Fig. 44 -

STANDARD REFERENCE POWDER DIFFRACTION
PATTERNS SELECTED FOR THIS WORK

<u>SUBSTANCE</u>	<u>PATTERN AND SOURCE</u>
α - Ti	JCPDS I 5-682
γ - TiH_{2-y}	EXPERIMENTALLY DETERMINED PATTERN FROM PROJECT BASE- LINE MATERIAL
KClO_4	EXPERIMENTALLY DETERMINED PATTERN FROM PROJECT BASE- LINE MATERIAL
KCl	JCPDS I 4-587
TiO_2 (rutile)	JCPDS I 21-1276

Fig. 45 - Experimentally Obtained Patterns Compared to Standard Patterns
(top and bottom), Each With CuK_{α} Radiation (Ni foil K_{β} filters)

Fig. 46 -

LABORATORY TITANIUM INTERNAL REFERENCE SAMPLE ANALYSES

DESCRIPTION OF MATERIAL	ANALYSIS: LATTICE PARAMETERS
ALFA VENTRON Ti POWDER: <325 MESH; 99% PURE	α -Ti $a_0 = 2.94769 \text{ \AA}$ $c_0 = 4.6877$
AREMCO Ti: <200 MESH; 99.7% PURE	α -Ti $a_0 = 2.9503$ $c_0 = 4.6799$
AREMCO Ti: 1-5 μm ; 99.7% PURE	α -Ti $a_0 = 2.95048$ $c_0 = 4.6811$
AREMCO Ti: <325 MESH; 99.7% PURE	α -Ti $a_0 = 2.9511$ $c_0 = 4.6853$

Fig. 47 -

LABORATORY "Ti H₂" INTERNAL REFERENCE SAMPLE ANALYSES

DESCRIPTION OF MATERIAL	ANALYSIS: LATTICE PARAMETERS
ALFA VENTRON TiH ₂ FROM SLA: "2 μm "; 3.30 wt % H	γ -TiH ₂ : $a_0 = 4.4596 \text{ \AA}$
ALFA VENTRON TiH ₂ FROM SLA: "7.2 μm "; 3.79 wt % H	γ -TiH ₂ : $a_0 = 4.4502$
ALFA VENTRON TiH ₂ (LOT NO. J4805 A)	γ -TiH ₂ : $a_0 = 4.4482$
ALFA VENTRON TiH ₂ (LOT NO. 4713A)	γ -TiH ₂ : $a_0 = 4.4533$
ALFA VENTRON TiH ₂ 1.88 μm	γ -TiH ₂ : $a_0 = 4.4533$
ALFA VENTRON TiH ₂ 1.88 μm	γ -TiH ₂ : $a_0 = 4.4305$

Fig. 48 -

COMPARATIVE LATTICE PARAMETERS FOR ACS-GRADE KClO₄
VS RECRYSTALLIZED SAMPLES

SAMPLE	ORTHORHOMBIC LATTICE PARAMETERS		
	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)
ACS-GRADE KClO ₄	8.86 ₁	5.667 ₇	7.253 ₉
ACS KClO ₄ - 1X	8.84 ₂	5.667 ₉	7.26 ₁
ACS KClO ₄ - 2X	8.84 ₂	5.67 ₁	7.254 ₈

Fig. 49 -

RESULTS FROM AN X-RAY ANALYSIS OF SIEVE FRACTIONS OF $\text{TiH}_{1.00}$

PARTICLE SIZE	PRESENCE OF α -Ti PHASE	PRESENCE OF TiH_{2-y} PHASE	TiH_{2-y} LATTICE PARAMETER (Å)	α -Ti LATTICE PARAMETERS (Å)	
				a_0	c_0
> 105 μm		✓	$a_0 = 4.418_4$	--	--
105 - 74		✓	4.419 ₄	--	--
74 - 63	QUESTIONABLE	✓	4.423 ₂	2.947 ₁	4.69 ₂
63 - 53	✓	✓	4.420 ₈	2.947 ₁	4.682 ₅
53 - 44	✓	✓	4.425 ₃	2.950 ₇	4.68 ₃
44 - 37	✓	✓	4.424 ₆	2.952 ₆	4.69 ₃
> 105		✓	4.420 ₂		

Fig. 50 -

 TiH_{2-y} LATTICE PARAMETERS OF $\text{TiH}_{1.60}$ SIEVE FRACTIONS

PARTICLE SIZE (μm)	TiH_{2-y} LATTICE PARAMETER (Å)
< 37	4.409 ₂
37-44	4.408 ₁
44-63	4.410 ₁
63-74	4.409 ₂
74-105	4.408 ₂
105-250	4.410 ₁

Fig. 51 -

LATTICE PARAMETERS OF CONSTITUENTS OF PARTICLE SIZED FRACTIONS OF $\text{TiH}_{0.19}$

CUT	CONSTITUENT(S)	LATTICE PARAMETERS OF CONSTITUENTS (Å)		
		α -Ti		γ - TiH_{2-y}
		a	c	a
1	α -Ti (MAJOR); γ - TiH_{2-y} (MINOR)	2.952 ₂	4.704 ₆	4.38 ₆
2	α -Ti (MAJOR); γ - TiH_{2-y} (MINOR)	2.953 ₁₈	4.706 ₂	4.37 ₆
3	α -Ti (MAJOR); γ - TiH_{2-y} (MINOR)	2.953 ₁	4.706 ₄	4.37 ₈
4	α -Ti (MAJOR); γ - TiH_{2-y} (MINOR)	2.953 ₁	4.707 ₄	4.36 ₆
5	α -Ti (MAJOR); γ - TiH_{2-y}	2.952 ₁	4.706 ₂	4.38 ₆
RESIDUE	α -Ti (MAJOR); γ - TiH_{2-y} (MINOR)	2.954 ₁	4.710 ₃	4.38 ₂

Fig. 52 - Plot of Lattice Parameters of the Cubic TiH_{2-y} Phase vs. the Overall Composition of TiH_x Samples

Fig. 53 - Lattice Parameter for Ti-Al Alloy Samples

Fig. 54 - Lattice Parameter for Ti-Al Alloy Samples

Fig. 55 -

**FURTHER PLANNED X-RAY DIFFRACTION SUPPORT OF
PYROTECHNIC PRODUCTION AND DEVELOPMENT:**

- CONTINUED ROUTINE ANALYSES IN SUPPORT OF OTHER TEAMS
- ELEVATED TEMPERATURE STUDIES OF TiH_x AND $KClO_4$
- DECOMPOSITION EFFECT OF X-RADIATION ON $KClO_4$
- DEBYE-SCHERRER LIMITS FOR MINOR CONSTITUENTS
- QUANTITATIVE DIFFRACTOMETRIC ANALYSIS OF TITANIUM-HYDROGEN SYSTEM

FIGS. 56-64 - VIEWGRAPHS FROM PRESENTATION BY J. W. REED

Fig. 56 -

Fig. 57 -

$$dq/dt = A (Q)^n e^{-E/RT}$$

$$Q_i = \left[1 - \frac{\int_0^{T_i} (dq/dt) dt}{\int_0^{\infty} (dq/dt) dt} \right]$$

$$dq/dt = \text{Energy Release (mcal mg}^{-1} \text{ sec}^{-1})$$

$$T = \text{Temperature (K)}$$

$$t = \text{Time}$$

$$R = \text{Gas constant (cal mole}^{-1} \text{ K}^{-1})$$

$$A = \text{Amplitude Factor (mcal mg}^{-1} \text{ sec}^{-1})$$

$$n = \text{Reaction Order}$$

$$E = \text{Activation Energy (Kcal mole}^{-1})$$

Fig. 58 - DSC Exotherm for $\text{KClO}_4/\text{TiH}_{0.65}$ (67/33)

Fig. 59 - DSC Exotherm for $\text{KClO}_4/\text{TiH}_{0.65}$ (67/33)

Fig. 60 - DSC Exotherm for $\text{KClO}_4/\text{TiH}_{0.65}$ (67/33)

Fig. 61 - DSC Exotherm for $\text{KClO}_4/\text{TiH}_{0.65}$ (67/33)

Fig. 62 - DSC Exotherm for $\text{KClO}_4/\text{TiH}_{0.65}$ (67/33)

Fig. 63 - DSC Exotherm for $\text{KClO}_4/\text{TiH}_{0.65}$ (67/33)

Fig. 64 -

KINETIC PARAMETERS

<u>K/MIN</u>	<u>40</u>	<u>80</u>	<u>160</u>	<u>320</u>
A	2.1×10^{18}	4.9×10^{17}	3.0×10^{17}	2.7×10^{17}
n	0.56	0.71	0.89	0.79
E	70	66	66	68

PARTIAL FIT

A	6.5×10^{24}	4.7×10^{24}	4.7×10^{24}	3.8×10^{24}
n	0.69	0.89	1.09	1.01
E	95	94	96	98

FIGS. 65-76 - VIEWGRAPHS FROM PRESENTATION BY T. M. MASSIS

Fig. 65 - $\text{TiH}_{0.65}/\text{KClO}_4$ Stability/Compatibility Status

Sample	Time (days)										
TiH _{0.65} /KClO ₄	7	50	103	173	243	307	367	460	547	730	
MM75-70											
100°C	2/2/77										
TiH _{0.65} /KClO ₄	1	8	15	30	50	98	182	239	359	728	
MM75-61											
100°C	7/7/77										
TiH _{0.65} /KClO ₄	50	239	728								
MM75-61	7/1/77										
TiH _{0.65} /KClO ₄	2	6	15	30	61	100	200				
Epoxy Charge											
Holder (50/50)	1/17/77										
120°C											
TiH _{0.65} /KClO ₄	30	60	90	150	210	270	360	450	540	728	
Compatibility											
Coupon Samples	2/14/77										
150°C - 3 Days											
120°C - Remainder											

Fig. 66 - Ti/KClO_4 Stability/Compatibility Status
CRT Configuration

Sample	Time (days)									
Ti/KClO ₄	7	15	28	49	235	306	418	540	728	
J-4705A									2/28/77	
100°C										
Ti/KClO ₄	3	7	14	21	38	67	120	210		
J-4705A									2/28/77	
120°C										
Ti/KClO ₄	1	3	7	14	20	38	66			
J-4705A								Complete		
160°C										
Ti/KClO ₄	1	3	7	10	14	20	33	67	96	
11-RS-14										Complete
160°C										

Fig. 67 - Component Aging Status

MC3004

$\text{TiH}_{1.9}/\text{KClO}_4$

50°C	11	24	102	225	485	730	
	[REDACTED]						2/27/77
100°C	8	24	102	225	485	730	
	[REDACTED]						2/9/77
150°C	8	24	102	225	485	730	
	[REDACTED]						1/20/77

MC3004

Ti/KClO_4

J-4705A	60°C	30	60	90	180	270	365	545	730	910	1095
		[REDACTED]									4/3/77
	100°C	30	60	90	180	270	365	545	730	910	1095
		[REDACTED]									4/3/77
	150°C	30	60	90	180	270	365	545	730	910	1095
		[REDACTED]									4/3/77

Fig. 68 - Stability of $\text{TiH}_x/\text{KClO}_4$ Chloride Formation

Fig. 69 - Stability of $\text{TiH}_x/\text{KClO}_4$ Rate of Cl^- Formation

Fig. 70 - Coupon Sample

Ceramic
$\text{TiH}_{0.64}/\text{KClO}_4$
TOPHET C
Epoxy
$\text{TiH}_{0.64}/\text{KClO}_4$
TOPHET C
Kapton
$\text{TiH}_{0.64}/\text{KClO}_4$
Kovar Wire
Epoxy
$\text{TiH}_{0.64}/\text{KClO}_4$
TOPHET C
Kovar Sheet

Test Conditions

150°C - 3 Days

120°C - 30, 60, 90, 150, 210, 270, 360, 450, 540, 720 Days

Fig. 71 - Coupon Sample

21-6-9 + Weld Bead
$\text{TiH}_{0.64}/\text{KClO}_4$
Metalized Ceramic
$\text{TiH}_{0.64}/\text{KClO}_4$
Brazed Kovar
$\text{TiH}_{0.64}/\text{KClO}_4$
Spring Material
$\text{TiH}_{0.64}/\text{KClO}_4$
Metalized Ceramic
$\text{TiH}_{0.64}/\text{KClO}_4$
21-6-9+Weld Bead

Test Conditions

150°C - 3 Days
 120°C - 30, 60, 90, 150, 210,
 270, 360, 450, 540,
 720 Days

Fig. 72 - Stability of $\text{TiH}_{0.65}/\text{KClO}_4$ in Coupon Configuration Chloride Formation

Fig. 73 - Compatibility of $\text{TiH}_{0.64}/\text{KClO}_4$ and Epoxy
Charge Holder Chloride Formation

Fig. 74 - Compatibility of $\text{TiH}_{0.64}/\text{KClO}_4$ and Epoxy
Charge Holder CO , CO_2 Evolution

Fig. 75 - Compatibility of $\text{TiH}_{0.64}/\text{KClO}_4$ and Epoxy
Charge Holder H_2O Evolution

Fig. 76 - Stability of Ti/KClO_4 in MC3004 Chloride
Formation

FIGS. 77-87 - VIEWGRAPHS FROM PRESENTATION BY T. M. MASSIS (2)

Fig. 77 - TMA - Thermomechanical Analysis

- Measurement of Vertical Displacement as a Function of Temperature or Time
- Utilizes a Movable Core Differential Transformer
- Provides a DC Output Proportional to Linear Displacement of the Core
- Sensitivity: 1.5×10^{-4} Inches per Inch of Chart Paper

Fig. 78 - System Description

Fig. 79 -

Fig. 80 - Expansion Coefficient $\times 10^{-6}/^{\circ}\text{C}$

	<u>-50°C to 0°C</u>	<u>0°C to 50°C</u>	<u>50°C to 100°C</u>	<u>100°C to 150°C</u>
$\text{TiH}_{0.65}/\text{KClO}_4$ Pellet Pressed at 10 kpsi	33	43	50	55
Epoxy Charge Holder Length Expansion	21	20	21	24
Epoxy Charge Holder Width Expansion	21	20	21	22

Fig. 81 -

Fig. 82 -

Fig. 83 -

Fig 84 -

Fig. 85 -

Fig. 86 -

Fig. 87 -

FIGS. 88-101 - VIEWGRAPHS FROM PRESENTATION BY L. W. COLLINS

Fig. 88 - Moisture Content of Ti/KClO_4

Fig. 89 - Moisture Content of $\text{TiH}_{0.65}/\text{KClO}_4$

Fig. 90 - Chloride Content of Ti/KClO_4

Fig. 91 - Chloride Content of $\text{TiH}_{0.65}/\text{KClO}_4$

Fig. 92 - Conclusion

- No Statistically Significant Increase in the Moisture or Chloride Content of Ti/KClO_4 or $\text{TiH}_{0.65}/\text{KClO}_4$.
- Blends Exposed to Relative Humidities from 25% to 75% for Periods Up to 1 Month.

Fig. 93 -

- "Decomposition temperature" was determined from the temperature of initial deflection of TG curves.
- Ti values were extrapolated to a zero heating rate by nonlinear La Grangian extrapolation.
- $\Delta\text{Ti} = \text{TiKClO}_4 - \text{TiKClO}_4 + \text{Metal Oxide}$

Fig. 94 -

- The catalytic efficiency varies with the oxide used.
- Less than 0.001% of metal oxides such as Co₂O₃ can perceptibly alter the decomposition temperature of KClO₄ by more than 25°C.

Fig. 95 -

Kinetics Calculations Based Upon the Following Assumptions:

- Decomposition reaction can be characterized by $\text{KClO}_4 \rightarrow \text{KCl} + 2\text{O}_2$
- Decomposition rate is slow enough that self heating is negligible.
- Decomposition reaction obeys first-order kinetics law.

Fig. 96 -

- Variation in the quantity of metal oxide shifts the pre-exponential factor.
- A correlation coefficient of 0.99 was obtained for the least-squares fit of the data.

Fig. 97 -

KINETICS CONSTANTS FOR
SOME POTASSIUM PERCHLORATE
METAL OXIDE SYSTEMS

METAL OXIDE	LOG A	ΔE (KCAL)
Co_2O_3	4.1	25
NiO	4.6	26
MnO_2	6.6	37
ZnO	10.8	50
TiO_2	10.8	52
pure KClO_4	13	63

Fig. 98 -

Conclusions:

1. Trace quantities of metal oxides produce large decreases in the activation energy of decomposition of potassium perchlorate.
 - a. Extrapolation to room temperature gives a negligible rate.
 - b. P-type semiconductors are generally better catalysts than N-type.
2. TiO_2 has a relatively small effect on the decomposition of KClO_4 .
3. Catalytic effects might influence performance more than long-term stability.

Fig. 99 - $\text{TiH}_{0.65}/\text{KClO}_4$ Stability Study Extends From
January to November 1977

Fig. 100 -

The feasibility of using Chemiluminescence for compatibility/stability studies is being investigated

Chemiluminescence, light emitted during some chemical reactions, can be used to infer the nature of the reaction.

Fig. 101 -

Possible advantages of using Chemiluminescence for compatibility/stability studies

1. Very slow reaction rates can be measured -- rates as low as 10^{-14} moles/year reported
2. Measurements made in hours vs. years required for present techniques
3. Measurements made at room temperature rather than at elevated temperature
4. Low cost equipment -- \$5K to \$10K

FIGS. 102-109 - VIEWGRAPHS FROM PRESENTATION BY A. C. MUNGER

Fig. 102 - MTS Tests

- Compared 150 vs. 170 mil L D. charge holders
- Compared ceramic vs. epoxy charge holders
- Evaluated effects of surface finish on compaction
- Evaluated pushout forces for loaded charge holders.

Fig. 103 -

MATERIAL
TESTING
SYSTEM
(MTS)
DIE SET

Fig. 104 -

Fig. 105 - Compaction in Various Charge Holders

Charge Holder Diameter (mil)	Force Transmitted Ratio (%)	Surface Finish μ in. (RMS)	Charge Holder
150	50	4	Molded Plastic
170	60	4	Molded Plastic
150	28	64	Ceramic
170	30	64	Ceramic
170	33	64	Molded Plastic

Fig. 106 - Comparison of Compaction

Batch	Force Trans. Ratio (%)	Density (mg/m^3)	Charge Holder
PO2040	29	1.82	Ceramic
PO3094	31	2.02	Ceramic
PO2040	28	1.83	Molded Plastic
PO3094	33	2.15	Molded Plastic

Fig. 107 - Material Characteristics

PO3094

33/67 blend of 1787ET and 1759ET

1787ET particle size (C^3)	0.9 μ
particle size zeiss	3.7 μ
BET surface area	1.1 m ² /gm
1759ET particle size zeiss	7.6 μ
BET surface area	0.2 m ² /g

PO2040

33/37 blend of 1675ET and 1759ET

1675ET particle size (C^3)	0.9 μ
BET surface area	8.1 m ² /g

Fig. 108 - Planned Material Analysis

- Characterize effect of particle size on compaction
- Characterize effects of surface area/topography on compaction
- Evaluate particle size ratios between fuel and oxidizer
- Record force relaxation after compaction
- Record forces generated during temperature changes.

Fig. 109 - Future Plans

- Temperature control of die
- More accurate measurement of displacement
- Bridgewire resistance monitoring during compaction
- HP-9825 data acquisition system
- HP-9825 process control

FIGS. 110-115 - VIEWGRAPHS FROM PRESENTATION BY W. E. SWARTZ

Fig. 110 - Initial Rates of Sulfur Segregation for Lot 16 Iron

$T (^{\circ}\text{C})$	$1000/T (\text{K}^{-1})$	V_i
200	1.486	8.2×10^{-4}
500	1.294	2.0×10^{-3}
600	1.145	9.28×10^{-3}
700	1.028	4.93×10^{-2}

Fig. 111 -

SURFACE COVERAGE BY SULFUR AS A FUNCTION OF TEMPERATURE FOR IRON POWDERS

Fig. 112 -

Fig. 113 -

Fig. 114 -

SURFACE COVERAGE BY CARBON AS A FUNCTION OF TEMPERATURE FOR IRON POWDERS

Fig. 115 -

RCA DATA FOR LOT 16 IRON POWDER

FIGS. 116-122 - VIEWGRAPHS FROM PRESENTATION BY A. B. DONALDSON

Fig. 116 -

Fig. 117 -

Differential Equation

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\rho q z}{k} e^{-Ea/RT} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad \begin{cases} a < r < \infty \\ t > 0 \end{cases}$$

Boundary Conditions

$$\Pi \alpha^2 \rho \hat{c} \frac{dT}{dt} = \frac{I^2 R}{\Pi a^2} - 2 \Pi a k \left. \frac{\partial T}{\partial r} \right|_a \quad \begin{cases} r = a \\ t > 0 \end{cases}$$

$$T = T_i \quad \begin{cases} r = a \\ t > 0 \end{cases}$$

$$\lim_{r \rightarrow \infty} T = T_i \quad \begin{cases} r \rightarrow \infty \\ t > 0 \end{cases}$$

Initial Conditions

$$T = \hat{T} = T_i \quad \begin{cases} 0 \leq r < \infty \\ t = 0 \end{cases}$$

Fig. 118 -

$$t \rightarrow t_{\text{ing}}, \quad \left. \frac{\partial^2 T}{\partial r^2} \right|_a, \quad \left. \frac{\partial T}{\partial r} \right|_a \rightarrow 0$$

$$\therefore \frac{dT}{dt} = \left. \frac{\partial T}{\partial t} \right|_a \quad \text{at } t = t_{\text{ign.}}$$

$$\Rightarrow \frac{qz}{c} e^{-Ea/RT^*} = \frac{I^2 R}{\Pi^2 a^4 \rho \hat{c}}$$

$$\Rightarrow T^* \Big|_a = \frac{Ea/R}{\left(\ln \frac{\Pi^2 a^4 \rho \hat{c} qz}{I^2 R} \right)}$$

Fig. 119 -

$$t_{\text{ign}} = t_{\text{inert}} + t_{\text{ad. expl.}}$$

$$\cong t_{\text{inert}}$$

$$t_{\text{inert}} = f^{-1}(T^*)$$

$$T^* = T_i + \frac{2Q\sigma^2}{\Pi^3 k} \int_0^\infty \frac{(1 - e^{-u^2}) \tau du}{u^3 \Delta(u)}$$

$$\Delta(u) = [u J_0(u) - \sigma J_1(u)]^2$$

$$+ [u Y_0(u) - \sigma Y_1(u)]^2$$

Short Time Approximation

$$T^* \cong T_i + \frac{\sigma Q}{z \Pi k} \left\{ \tau - \frac{4\sigma}{3\sqrt{\pi}} \tau^{3/2} \right\}$$

Long Time Approximation

$$T^* \cong T_i + \frac{Q}{4\pi k} \left\{ \ln(4\tau) - \gamma \right\}$$

Fig. 120 -

$$\sigma = 1.0$$

Fig. 121 -

Fig. 122 -

Hot Wire Ignition of $\text{TiH}_{1.9}\text{KClO}_4$ with 2 mil dia.
Tantalum Bridgewire in MC3004 Hardware

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