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**Industrial Applications of Powder
X-Ray Diffraction Analysis to the
 TiH_x - KClO_4 Pyrotechnic System**

**Don B. Sullenger, Ralph R. Eckstein,
and Richard S. Carlson**

June 14, 1977

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ABSTRACT

Powder X-ray diffraction techniques were extensively applied in a pyrotechnic materials development project involving the $\text{TiH}_x\text{-KClO}_4$ system. They were utilized in the evaluation of locally synthesized TiH_x materials to assist in evolving the best method for preparing such hydride materials. Once that method was fixed, X-ray diffraction made a contribution towards material specification for the project in that it afforded baseline data for TiH_x and KClO_4 starting materials, and especially in the determination and detailed characterization of the phases present in their various blends. Such methods concurrently afforded routine support for other project teams investigating container and bridgewire corrosion phenomena, material and device handling and storage factors, alternative milling and blending effects, particle size classification consequences, reaction product identification, etc.

A 12-kW rotating anode X-ray generator was used to good advantage in the effort. It yielded adequate diffraction photographic exposures from tiny specimens in a few minutes time, and thus, made practicable some investigations which otherwise would not have been possible.

Aside from the immediately practical support provided for the project a reference pattern was obtained for the nonstoichiometric fluorite-structured $\gamma\text{-TiH}_{2-y}$ phase which proved superior to any found in the literature. Also a quality lattice parameter as a function of stoichiometry curve was deduced from the repeated phase analyses. Detection limits of minor amounts of various substances often encountered in the course of the project were also assessed.

INTRODUCTION

A relatively large pyrotechnic materials development and production program has been in progress for somewhat over 2 yr to produce quantities of powdered TiH_x materials such that appropriate TiH_x-KClO_4 blends would be both statically insensitive and reliably ignitable with a hot wire. Preliminary indications were that some composition(s) with $0 < x < 2$ would be required. Such material(s) should be reproducibly preparable and routinely characterizable.

Several teams of diverse technical interest were involved in the effort. X-ray diffraction analysis support for the project was enlisted in its formative stages, and the powder diffraction technique was utilized extensively throughout the course of the operation. This is an account of that diffraction work - the techniques employed, the data obtained, how such information aided the program, and some of the fundamental knowledge thus far gained of the Ti-H system and of $KClO_4$.

Extensive fundamental crystalline state information concerning both the Ti-H system and $KClO_4$ was available prior to this project (1) - (14), so the X-ray diffraction task was largely one of using that information to best advantage in developing, producing, and testing the desired materials. One aspect called for providing baseline data for starting constituents and blends to enable realistic materials specifications to be written for the intended applications. Another focus was on hydride homogeneity evaluations. A third interest was the characterization of solid combustion products, possibly contributory to an understanding of the TiH_x-KClO_4 pyrotechnic reaction mechanism, its control, and efficient utilization. Concurrent with these topics was an assignment to provide routine support of other investigative teams. Opportunities to increase fundamental knowledge of the reactant substances were to be exploited as time permitted.

Stemming largely from extensive powder diffraction experience with radioactive and/or chemically reactive materials, a safe, reliable handling and storing technique had been developed in this laboratory to obtain definitive solid phase information from specimens in the order of 5-mg amounts. (15) That this method proved directly applicable to the pyrotechnic samples was fortunate, for it avoided the appreciable danger arising from manipulation of these sensitive materials in the gram quantities required by many other analytical methods.

EXPERIMENTAL TECHNIQUES

Particle sizes of the powdered materials submitted for analysis were generally fine enough (0.1 - 100 μm diameter) to afford their random packing into the 0.3 - 0.5 mm (internal diameter) quartz capillaries of 20 mm length used for diffraction exposures. Thus no additional grinding of the substances was required. Except in special cases no attempt was made to restrict or exclude air exposure of the samples as they showed no reaction with the laboratory air during handling. The open ends of capillaries were closed with grease or wax. Specimens so prepared (15) yielded Debye-Scherrer diffraction photographs of moderate quality in 6 - 12 hr when subjected to the CuK_α (Ni foil K_β filtered)

X-radiation produced with a GE XRD-5 fixed anode generator operating at 40 kV and 20 mA. Equivalent photographs were obtained in 10-20 min with a 12 kW Rigaku RU 200-PL rotating anode generator operating in the normal focus mode with a copper target at 50 kV and 200 mA. Eventually, as a result of its greatly reduced exposure time, the rotating anode generator came to be used almost exclusively for these diffraction analyses. While the TiH_x photographs exhibited significant fluorescence background blackening and a lack of observable back-reflection K_α -doublet splitting, they displayed 10 or more lines sharp enough for four to five digit interplanar spacing determinations. In general nearly pure Ti samples did exhibit K_α -doublet splitting and yielded perhaps another digit of lattice-parameter accuracy. Other radiations (particularly FeK_α) were tried without significant background reduction.

From the visually measured diffraction line positions on the photographic patterns obtained with 114.6-mm diameter Electronics and Alloys cameras interplanar spacings were computed via the PDP 8/I computer program DSPC (16), which affords the application of a single camera correction-film shrinkage or expansion parameter. A visually estimated intensity scaled as 1,2,..., relative to a strongest line value of 10, was associated with each spacing. With the aid of another PDP 8/I computer program, least squares fitted lattice parameters were obtained in the diffraction laboratory for indexed cubic patterns such as those of the TiH_{2-y} phases. Lattice parameters for noncubic crystalline components, such as for hexagonal α -Ti or orthorhombic KClO_4 , were calculated via a more general IBM 360/50 program. Both of these programs utilize equally weighted interplanar spacings (d-spacings) from indexed reflections to obtain lattice parameters. Overall standard deviations and individual diffraction angle (i.e., 2θ) drifts and residuals are printed out so as to afford a decision criterion for inclusion or exclusion of particular reflections in a given computation. All distance and length errors utilized in the work and quoted herein are given to $\pm 2\sigma$, i.e., at a 95% confidence level. When necessary, reflection indices were generated and their corresponding d-spacings computed from given lattice parameters via another IBM 360/50 program.

SELECTION OF STANDARD REFERENCE PATTERNS

Selection of standard reference patterns was an initial concern of the diffraction work. The experimental pattern for less than 325 mesh Aremco titanium agreed quite well with the JCPDS pattern for α -Ti (i.e., I 5-682) (17), so that pattern was adopted as a standard. That Aremco titanium was employed for this test purpose because it was used as a starting material for many TiH_x preparations at Mound.

Similarly the project's baseline KClO_4 from Barium and Chemical Corp. agreed rather well with JCPDS pattern I 7-211 (18) except that the experimental pattern contained several additional weak lines of shorter d-spacing. The possible d-spacings for KClO_4 were calculated (19) using the orthorhombic lattice parameters $a = 8.857 \text{ \AA}$, $b = 5.663 \text{ \AA}$, $c = 7.254 \text{ \AA}$, given with the file pattern. It was found that all the additional lines could be identified with lines of the theoretically possible set. The complete experimental pattern, thus indexed, is presented in Table 1. Subsequent least squares computation of lattice

Table 1

POWDER DIFFRACTION PATTERN FOR BASELINE KClO_4

hkl^a	d (Å)	I/I_0	hkl^a	d (Å)	I/I_0	hkl^a	d (Å)	I/I_0
101	5.634	3	024	1.524	1	723	1.042	2
011	4.479	5	124	1.502	2	820	1.031	1
201	3.783	2	521	1.469	1	615	1.017	1
002	3.616	4	133	1.458	1	145	1.007	2
210	3.478	10	105	1.432	1	236	0.9926	1
102	3.349	4	423	1.412	2	733	0.9640	1
211	3.131	10	611	1.399	3	060	0.9428	1
112	2.902	9	513	1.383	1	407	0.9377	1
202	2.805	7	324	1.356	2	445	0.9213	1
121	2.508	7	215	1.338	1	644	0.8902	3
220	2.392	1	241	1.325	2	218	0.8769	1
103	2.344	1	305	1.301	1	840	0.8716	1
221	2.270	2	134	1.292	1	263	0.8626	1
122	2.161	8	523	1.272	3	355	0.8553	1
401	2.108	9	225	1.238	1	607	0.8483	1
410	2.063	1	143	1.210	2	617	0.8385	1
321	1.974	1	440	1.193	1			
303	1.870	3	441	1.176	2			
123	1.798	2	533	1.140	2			
313	1.772	2	434	1.127	1			
420	1.734	1	235	1.113	2			
114	1.690	3	713	1.100	2			
511	1.642	3	251	1.083	1			
323	1.559	2	335	1.071	2			

^aIndices from JCPDS File No. I 7-211 plus possible lines calculated from the JCPDS lattice parameters.

parameters yielded values of $a = 8.857 \pm 0.007$ Å, $b = 5.664 \pm 0.004$ Å, $c = 7.254 \pm 0.004$ Å for this material. The experimental pattern was tentatively selected as a reference pattern early in the diffraction work. However, comparisons of numerous experimental patterns with both of these patterns revealed little to choose between them. The experimental pattern proved to be the more useful during the course of the work largely owing to the fact that that material was so widely used in preparation of pyrotechnic blends for testing. Thus analyses for reaction completion, etc., involved direct comparisons of complete or fragmentary patterns of this same material.

Comparisons of reagent grade KCl and TiO_2 (rutile) showed good agreement respectively with JCPDS patterns I 4-587 (19) and I 21-1276 (20). Thus those patterns were adopted as standards. There were no project-designated baseline KCl and TiO_2 materials in as much as they were likely reaction products and not reactants.

The project's baseline "TiH₂" was a quantity of Alfa Ventron Corp. material obtained via Sandia Laboratories at Albuquerque, N. Mex. (SLA), and of nominal 2- μ m particle size. Mound elemental analysis of this material indicated 3.85 wt % hydrogen, corresponding to a formula of TiH_{1.90}. This substance yielded a relatively high-quality photograph whose lines agreed but poorly with JCPDS pattern I 9-371 (21) then (late 1974) listed for supposed TiH₂. Inspection of that JCPDS pattern revealed that it was of generally inferior quality in that it is given to only three-decimal accuracy, and three of its major lines are indicated as being overlapped with α -Ti lines. Another sample of Alfa Ventron high purity "TiH₂", also obtained via SLA, but of nominal 7.2- μ m particle size, gave a sharper diffraction pattern than the other sample. It was found to contain 3.99 wt % H, corresponding to a formula of TiH_{1.97}. Owing to its superior quality that pattern was taken as a reference pattern for the nonstoichiometric, cubic γ -TiH_{2-y} phase in all subsequent analyses. When its d-spacings were indexed via the TiD_{1.971} indices given by Sidhu, et al. (12), a very reasonable cubic lattice parameter of $a = 4.450 \pm 0.002$ Å was obtained for this material. When Mound Laboratory obtained the 1975 version of the JCPDS file, including Set Number 25, we noted that the pattern for TiH_{1.924} at 28°C, due to Crane, et al., (22) had been added to the inorganic file as I 25-983 (23). This pattern agrees quite well with that from the 7.2- μ m Alfa Ventron material, but it contains only five lines. The three patterns are arranged in Table 2 for comparative purposes. A rather thorough search of the literature has convinced us that the reference pattern selected for our work is superior to any published in the literature. Thus we are submitting it to the JCPDS for inclusion in their files.

A list of the standard reference patterns adopted for this supporting analytical work are listed in Table 3.

PROVIDING BASELINE DATA FOR STARTING MATERIALS AND BLENDS

Numerous TiH_x samples prepared at Mound were subjected to X-ray diffraction analyses. For each the d-spacings were calculated, the components were identified as far as possible (nearly always accomplishable), and from their indexed d-spacings the lattice parameters were calculated for each constituent. In the first preparations, lines characteristic of the α -Ti pattern were detectable only in those TiH_x patterns for which $0.5 \leq x \leq 1.5$, such unique lines diminishing regularly in intensity throughout that compositional range. The cubic γ -TiH_{2-y} phase was present in those too and was the only phase found in samples richer in hydrogen. No appreciable change in lattice size was observed in the α -Ti phase regardless of overall hydrogen content of the sample. As the overall hydrogen content grew, however, the lines of the γ -TiH_{2-y} phase increased regularly in intensity, and its lattice expanded as the ideal fluorite phase composition of TiH₂ (6) was approached. These facts were in general agreement with the known characteristics of the Ti-H system at room temperature and somewhat above (1)-(14). General characteristics of these patterns and their trends are illustrated in the d-spacing-intensity plots of Figure 1, where the reference patterns of α -Ti and γ -TiH₂ have been added for comparison. The analyses were not quantitative, so the intensity trends are not exact.

Table 2

EXPERIMENTAL AND JCPDS REFERENCE
POWDER DIFFRACTION PATTERNS FOR TiH_{2-y}

<u>Alfa Ventron $\text{TiH}_{1.97}$</u>			<u>$\text{TiH}_{1.924}$ [JCPDS I 25-983]</u>			<u>TiH_2 [JCPDS I 9-371]</u>		
<u>hkl^a</u>	<u>d (Å)</u>	<u>I/I</u>	<u>hkl</u>	<u>d (Å)</u>	<u>I/I</u>	<u>hkl</u>	<u>d (Å)</u>	<u>I/I</u>
111	2.5560	100	111	2.569	100	101	2.50	50
200	2.2139	30	200	2.224	25	110 (+ α -Ti)	2.20	100
220	1.5678	70	220	1.573	35	002	2.10	10(?)
311	1.3382	50	311	1.342	25	200	1.55	30
222	1.2809	30	222	1.285	8	211 (+ α -Ti)	1.33	40
400	1.0926	10				103 (+ α -Ti)	1.27	10
331	1.0188	30				301	1.01	10
420	0.9937	20						
422	0.9081	20						
333}	0.8561	20						
511}								

^a Indexed by means of $\text{TiD}_{1.971}$, Sidhu, et al (12).

FIGURE 1 - Experimentally obtained patterns compared to standard patterns (top and bottom), each with CuK_{α} radiation (Ni foil K_{β} filters).

Table 3

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 7.2- μm Alfa Ventron $\text{TiH}_{1.97}$, Project Base- line Material (listed in Table 2)
KClO	Experimentally determined pattern from Barium and Chemical KClO_4 , Project Baseline Material (listed in Table 1) [Note: JCPDS I 7-211 is virtually of equal usefulness]
KCl	JCPDS I 4-587
TiO_2 (rutile)	JCPDS I 21-1276

Lattice parameters were generally obtainable to four digits with $\pm 2\sigma$ values of one to four in the last digit. The lattice parameter shift with stoichiometry was in the third place. However, attempts to construct a plot of this lattice parameter as a function of overall composition or of stoichiometry of the γ - TiH_{2-y} phase were frustrated by the variability of the preparations.

The magnitude of the TiH_x production problems became more evident as comparative analyses of commercial, supposedly high-purity, materials revealed notable differences in their lattice sizes. Table 4 shows results of some diffraction analyses of various high purity Ti and " TiH_2 " samples. The " TiH_2 " samples, especially, have marked variations in lattice parameters. (Duplicate samples of the same material showed close agreement, however).

The previous section indicated the lattice parameters for the baseline KClO_4 and gave its extensive diffraction pattern. Exemplary of KClO_4 investigations was one occasion in which ACS-grade KClO_4 was compared with recrystallized samples of the same material. Resulting patterns exhibited no significant differences between one another. Respective orthorhombic lattice parameters obtained for the ACS-grade and the two recrystallized samples are given in Table 5. Apparently recrystallization did not appreciably affect the ACS-grade KClO_4 . Whether the recrystallization conditions were optimal for formation of quality crystals was not investigated, but the declining quality of the lattice parameter accuracy raises suspicion.

Table 4

LABORATORY INTERNAL REFERENCE SAMPLE ANALYSES

<u>Description of Material</u>	<u>Analysis; Lattice Parameters</u>
Alfa Ventron Ti Powder: <325 mesh; 99% pure	α -Ti $a = 2.9476 \pm 0.0009\text{\AA}$ $c = 4.687 \pm 0.002$
Aremco Ti: <200 mesh; 99.7% pure	α -Ti $a = 2.950 \pm 0.003$ $c = 4.679 \pm 0.009$
Aremco Ti: 1-5 μm ; 99.7% pure	α -Ti $a = 2.9504 \pm 0.0008$ $c = 4.681 \pm 0.001$
Aremco Ti: <325 mesh; 99.7% pure	α -Ti $a = 2.951 \pm 0.001$ $c = 4.685 \pm 0.003$
Alfa Ventron TiH ₂ from SLA: "2 μm "; 3.30 wt % H	γ -TiH ₂ : $a = 4.459 \pm 0.006$
Alfa Ventron TiH ₂ from SLA: "7.2 μm "; 3.79 wt % H	γ -TiH ₂ : $a = 4.450 \pm 0.002$
Alfa Ventron TiH ₂ (Lot No. J4805 A)	γ -TiH ₂ : $a = 4.448 \pm 0.002$
Alfa Ventron TiH ₂ (Lot No. 4713A)	γ -TiH ₂ : $a = 4.453 \pm 0.003$
Alfa Ventron TiH ₂ 1.88 μm	γ -TiH ₂ : $a = 4.453 \pm 0.003$
Alfa Ventron TiH ₂ 1.88 μm	γ -TiH ₂ : $a = 4.430 \pm 0.005$

Table 5

COMPARATIVE LATTICE PARAMETERS FOR ACS-GRADE KC10₄
VS RECRYSTALLIZED SAMPLES

	<u>Orthorhombic Lattice Parameters</u>		
	<u>a($\text{\AA}$)</u>	<u>b($\text{\AA}$)</u>	<u>c($\text{\AA}$)</u>
ACS-Grade KC10 ₄	8.86 $\pm$ 0.01	5.667 $\pm$ 0.007	7.253 $\pm$ 0.009
ACS KC10 ₄ - Recrystallized once	8.84 $\pm$ 0.02	5.667 $\pm$ 0.009	7.26 $\pm$ 0.01
ACS KC10 ₄ - Recrystallized twice	8.84 $\pm$ 0.02	5.67 $\pm$ 0.01	7.254 $\pm$ 0.008

The photographic powder diffraction technique as applied produced reliable data from minute samples of the pyrotechnic starting materials. It was capable of providing one day turnaround times when the need was urgent. On one occasion six sequential analyses were finished in one day. Duplicates were not necessary for most analyses in that agreement between pairs of the same sample was well within the 95% confidence error limits adopted for lattice parameters. This method was thus adopted as one of the standard analytical techniques for the pyrotechnic project.

DETECTION LIMITS FOR MINOR AMOUNTS OF α -Ti IN γ -TiH₂ AND VICE VERSA

The number of project diffraction samples did not afford time to determine detection limits for various minor phases until some months after initiation of the work. The importance that this technique eventually assumed in the pyrotechnic project justified some effort to find such limits for α -Ti, γ -TiH_{2-y} mixtures, however.

Powdered mixtures of titanium powder and TiH_{1.94} containing 0, 3, 5, 10, 90, 95, 97, and 100 wt % of the former were subjected to typical 20-min diffraction exposures. The γ -TiH_{1.94} could be detected at 3 wt % or higher concentrations, but α -Ti could not be detected until present at 5 wt % or higher levels. Lattice constants of the former were obtainable with 95% confidence to ± 0.04 Å at the 10% level, and lattice constants of the latter were obtainable at ± 0.02 Å at the 3% level. Table 6 presents a summary of the data underlying these generalizations.

Similar limits for α -Ti or γ -TiH_{2-y} in the presence of KClO₄ and vice versa have not been ascertained. KClO₄ tends to be well-crystallized and thus gives a good, many-lined pattern which dominates patterns from its mixtures. However, at the levels used for most pyrotechnic blends (35 - 70 wt % Ti or TiH_x with the remainder KClO₄), there was no difficulty in detecting six or more unique lines for Ti or TiH_{2-y}. Thus their identification was not a major problem and their lattice parameters could be obtained with moderate accuracy.

ASSISTING IN FINDING A SUPERIOR TiH_x PREPARATIVE METHOD

A major initial concern of the pyrotechnic project was finding a method for producing sufficient quantities of the TiH_x hydrides having constituents as homogeneously distributed as possible. In early preparations, microphotographic techniques, among others, had indicated that the constituent phases were not homogeneously distributed among the particles. There was some evidence that the distribution of constituents might be correlated with particle size.

In one study a sample of TiH_{1.00} material was sieved into varying-sized fractions to determine whether a correlation existed between particle size and phase content. X-ray diffraction analysis of the fractions yielded the results in Table 7. Both α -Ti and γ -TiH_{2-y} were detected in fractions with particle sizes less than 63 μ m. The TiH_{2-y} alone was detected in fractions with particle sizes larger than 75 μ m, which indicated that the largest sized α -Ti particles were smaller than some γ -TiH_{2-y} particles. Cubic lattice parameters for γ -TiH_{2-y} varied slightly over the particle size ranges, and a similar slight drift occurred for α -Ti. When the greater than 105- μ m sample was pulverized by ball milling to see whether such processing affected constituent composition and/or constituent lattice parameters, X-ray analysis revealed no significant variation of either.

Table 6

DETECTION OF MINOR AMOUNTS OF α -Ti IN γ -TiH_{2-y} AND VICE VERSA

Wt % α -Ti	Wt % γ -TiH _{1.94}	Observed α -Ti (No. lines)	Observed γ -TiH _{1.94} (No. lines)	Lattice Parameters (Å)		
				α -Ti		γ -TiH _{1.94}
				a	c	a
100	0	✓(25)		2.9523 ± 0.0006	4.705 ± 0.002	
97	3	✓(20)	✓(4)	2.953 ± 0.001	4.706 ± 0.004	4.43 ± 0.02
95	5	✓(20)	✓(4)	2.953 ± 0.001	4.705 ± 0.005	4.43 ± 0.03
90	10	✓(18)	✓(3)	2.953 ± 0.002	4.704 ± 0.008	4.42 ± 0.09
10	90	✓ (8)	✓(10)	2.95 ± 0.02	4.72 ± 0.04	4.450 ± 0.004
5	95	✓ (4)	✓(10)	Didn't calculate - too few lines		4.42 ± 0.12
3	97		✓(10)	---	---	4.450 ± 0.003
0	100		✓(10)	---	---	4.453 ± 0.005

Table 7

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 ($\text{\AA}$)	α -Ti Lattice Parameters ($\text{\AA}$)	
				a	c
>105 μm		✓	$a_0 = 4.418 \pm 0.004$	---	---
105 - 74		✓	4.419 ± 0.004	---	---
74 - 63	Questionable	✓	4.423 ± 0.002	2.947 ± 0.001	4.69 ± 0.02
63 - 53	✓	✓	4.420 ± 0.008	2.947 ± 0.001	4.682 ± 0.005
53 - 44	✓	✓	4.425 ± 0.003	2.950 ± 0.007	4.68 ± 0.03
44 - 37	✓	✓	4.424 ± 0.006	2.952 ± 0.006	4.69 ± 0.03
>105 ^a		✓	4.420 ± 0.002		

^aOriginal largest particle size fraction ball milled to see whether such treatment affected its composition and/or the lattice parameters of its component phases.

As preparative techniques improved, particle inhomogeneity noticeably diminished. Detailed changes in preparative methods are not a concern of this report and will not be discussed. Standardized X-ray diffraction techniques were utilized to guide product improvement.

Illustrative of the guidance, a sample (of overall composition $\text{TiH}_{1.60}$), produced at Mound by the improved technique, was similarly sieved into various particle size fractions and subjected to X-ray analysis. This time all fractions consisted solely of $\gamma\text{-TiH}_{2-y}$. Lattice parameters for the fractions are displayed in Table 8. These data reveal that the newer preparative method yielded material of very uniform stoichiometry as well as of identical phase composition. Owing to this finding among others, the method was adopted for subsequent preparations and has remained substantially unchanged since then.

Table 8

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

Particle Size (μm)	TiH_{2-y} Lattice Parameter ($\text{\AA}$)
<37	4.409 ± 0.002
37-44	4.408 ± 0.001
44-63	4.410 ± 0.001
63-74	4.409 ± 0.002
74-105	4.408 ± 0.002
105-250	4.410 ± 0.001

One other aspect of this analysis should be noted. All the results of Table 8 were obtained within one day as they were much needed for an opportune program review. The rotating anode X-ray generator, which afforded sequential 20-min exposures to gather the diffraction data, enabled all six patterns to be obtained in slightly over 2 hr, a total time in the order of one third that required to obtain a single exposure for this sized sample with a fixed anode apparatus. On several other occasions the power of the rotating anode made possible analyses which otherwise would not have been feasible.

SUPPORTING OTHER TEAMS

Perhaps more pyrotechnic samples were analyzed via X-ray diffraction in support of other investigative teams than for any other purpose. These analyses spanned the scope of the project. Several other methods of analysis, being of a comparative nature, regularly made use of the crystal geometry and dimensions determined by the polycrystalline methods. A case in point is that of nuclear magnetic resonance (NMR) which made use of detailed lattice parameters and atomic geometry for particular materials.

The X-ray diffraction analyses also often afforded answers to specific points troubling other teams. A few representative illustrations should suffice to indicate the variety of those applications.

Pyrotechnic reaction residues nearly always appeared heterogeneous. In such cases a portion representative of the entire sample required investigation as well as each discernably different type of particle. Sometimes particles were noncrystalline, i.e., glassy, and did not yield a pattern.

One reaction residue was found to contain some glassy material, a white opaque powder, and a grayish granular material. Little could be told concerning the glassy substance via the large angle X-ray diffraction being employed. The white powder was easily identified as a two-phase mixture of the rutile polymorph of TiO_2 (via JCPDS pattern I 21-1276) (20) and a KCl (via JCPDS pattern I 4-587) (19). The gray substance consisted primarily of TiO_2 ; however, it contained several weak lines from a second phase. Identification of that phase was not certain, but the lines were akin to those from $\text{Ca}_3\text{Si}_3\text{O}_9 \cdot \text{H}_2\text{O}$. A representative overall sample produced no additional lines. Such results underscore the heterogeneous character of the pyrotechnic reactions and indicate the likelihood for reaction of the pyrotechnic substances with adjacent firing electrodes, containers, and seals.

In another solid residue sample (from a missfire incident), the presence of TiH_{2-y} , KClO_4 , and KCl were definitely established; but no TiO_2 was detected. No evidence was found either for a reaction with container materials or bridgewires. Line overlap had to be considered to rationalize the complicated diffraction pattern obtained. The dominating complex pattern of KClO_4 together with the pattern for the also-present TiH_{2-y} left only two unique KCl lines. However, to match intensities correctly it was necessary to include contributions from overlapped KCl lines, attesting also to its presence.

To assist differential thermal analysis (DTA) investigations, comparative X-ray diffraction photographs were taken of two contrastingly treated samples, each composed of a blend of 33 wt % TiH_{2-y} and 67 wt % KClO_4 . One sample had been heated and held at 440°C for 2.5 hr, while a control sample had been kept at ambient temperature. Both were found to contain TiH_{2-y} and KClO_4 . However, there were differences in their patterns. The heated sample yielded a pattern with KClO_4 lines markedly reduced in intensity, leading to fewer lines - 29 vs 37 for the untreated specimen. The TiH_{2-y} pattern, on the other hand, did not suffer an intensity diminution, leading to stronger relative intensities in the heated material. This indicated that the KClO_4 , on being heated, decomposed instead of reacting with the TiH_{2-y} . Such an interpretation was helpful in assessing previously mystifying DTA results and was subsequently corroborated via comparative ClO_4^- , ClO_3^- , Cl^- analyses.

The compatibility of the Ti-KClO_4 blend constituents with one another, their bridgewires, their container materials, etc. was the focus for an investigation of a pyrotechnic device which had been assembled for 5 yr. Only $\alpha\text{-Ti}$ and KClO_4 with normal lattice parameters were found in the remaining powdered charge material. There was no indication of solid decomposition products, such as KCl and/or TiO_2 , nor any contaminant.

That is to say, the device's pyrotechnic blend constituents, bridgewire substances, and container materials were mutually compatible for a 5-yr period at least.

In the course of the pyrotechnic program it became evident that many processing factors and material characteristics might have important ramifications on the performance of a blend incorporated into a device. At one stage there was a tight deadline for selecting the most favorable materials for utilization in a component. A coordinated effort to characterize TiH_x samples which had undergone various combinations of ball milling, dehydriding, particle size classifications, etc., to produce specific particle sizes, hydrogen contents, surface areas, etc., then prominently shaped the powder X-ray diffraction work.

An example will illustrate an analysis in that coordinated effort. Table 9 presents the identification and lattice parameters of phases in cuts from three hydride samples which had undergone particle size classifications. These cuts had been independently analyzed for surface area, overall hydrogen content, overall oxygen content, etc. With increasing cut number and increasing particle size, the listed fractions had shown a decreasing oxygen and an increasing hydrogen content. The X-ray analyses reveal no significant lattice parameter shifts for either constituent with changing particle size, indicating no change in stoichiometry of the $\gamma-TiH_{2-y}$ phase certainly. This supported the hypothesis that individual particles had roughly equal depth layers of titanium oxide of the same composition (whatever that might be) on their surfaces regardless of their diameters. Such oxide shells will constitute larger portions of the volumes of the smaller particles, and, consequently, will engender larger oxygen and smaller hydrogen contents. Whatever the oxide form it was not detectable in the diffraction patterns, possibly because it was so poorly crystallized and/or finely divided and probably because it was in such small concentration (1-3 wt %). Results from electron spectroscopy for chemical analysis (ESCA) supported this hypothesis. Such considerations, among others, were useful in evolving characteristics for a successful material for the required device utilization.

OBTAINING A TiH_{2-y} CUBIC LATTICE PARAMETER AS A FUNCTION OF COMPOSITION CURVE FOR TiH_x

Since lattice parameter data for the cubic TiH_{2-y} phase had been extensively utilized in this project and since many apparent stoichiometries of that phase had been prepared, it seemed natural to attempt to produce a curve for that parameter as a function of x for the powdered TiH_x material. Irving and Beevers (2) obtained such a curve for bulk titanium hydride specimens (2 x 0.125 x 0.125 in.) in the composition range $TiH_{1.53}$ to $TiH_{1.99}$, utilizing metallographic observation to corroborate the presence of one or more phases in their polycrystalline blocks.

Table 9

LATTICE PARAMETERS OF CONSTITUENTS OF PARTICLE SIZE
CLASSIFIED HYDRIDE MATERIALS OF POSSIBLE DEVICE COMPONENT USEFULNESS

Sample	Cut	Constituent(s)	Lattice Parameters of Constituents (Å)		
			α -Ti		γ -TiH ₂
			a	c	a
TiH _{1.85}	1	TiH _{2-y}			4.450 ± 0.008
	2	TiH _{2-y}			4.449 ± 0.006
	3	TiH _{2-y}			4.447 ± 0.003
	4	TiH _{2-y}			4.449 ± 0.006
	Residue	TiH _{2-y}			4.449 ± 0.008
TiH _{0.19}	1	α -Ti (major); γ -TiH _{2-y} (minor) ^a	2.952 ± 0.002	4.704 ± 0.006	4.38 ± 0.06
	2	α -Ti (major); γ -TiH _{2-y} (minor)	2.9531 ± 0.0008	4.706 ± 0.002	4.37 ± 0.06
	3	α -Ti (major); γ -TiH _{2-y} (minor)	2.953 ± 0.001	4.706 ± 0.004	4.37 ± 0.08
	4	α -Ti (major); γ -TiH _{2-y} (minor)	2.953 ± 0.001	4.707 ± 0.004	4.36 ± 0.06
	5	α -Ti (major); γ -TiH _{2-y} (minor)	2.952 ± 0.001	4.706 ± 0.002	4.38 ± 0.06
	Residue	α -Ti (major); γ -TiH _{2-y} (minor)	2.954 ± 0.001	4.710 ± 0.003	4.38 ± 0.02
TiH _{0.70}	1	α -Ti; γ -TiH ₂	2.974 ± 0.034	4.74 ± 0.07	4.392 ± 0.008
	2	α -Ti; γ -TiH ₂	2.946 ± 0.018	4.65 ± 0.07	4.396 ± 0.003
	3	α -Ti; γ -TiH ₂	2.943 ± 0.014	4.65 ± 0.05	4.390 ± 0.004
	4	α -Ti; γ -TiH ₂	2.948 ± 0.012	4.66 ± 0.05	4.404 ± 0.007

^aOnly four unique lines are observable in each experimental pattern for the TiH_{2-y} component, which accounts for the relatively poor 2 σ value on each refined lattice parameter.

Samples selected for measurement were prepared by the best hydriding method, that of withdrawing H_2 from powdered TiH_2 until the desired lower composition was obtained. Photomicrographic inspection indicated that this method produced uniform phase distribution among particles.

Figure 2 is a graph of the results with plotted points an average of duplicate specimens of each sample. The error limits are $\pm 2\sigma$ as employed throughout the present work. Samples of composition, $TiH_{0.33}$ to $TiH_{1.32}$ contained both α -Ti and TiH_{2-y} ; those of composition $TiH_{1.44}$ through $TiH_{1.90}$ contained only TiH_{2-y} . There has been no correction for the 1-3 wt % oxygen content. Therefore x for the TiH_x composition is undoubtedly higher than indicated on the graph. Work is continuing with regard to such corrections. The work of Irving and Beevers indicated a lattice parameter expansion from 4.407 Å to 4.434 Å in proceeding from a composition to $TiH_{1.53}$ to $TiH_{1.90}$, with an accuracy of ± 0.001 Å estimated via Nelson-Riley extrapolation. Their samples contained only approximately 0.05 wt % oxygen which again indicates the need for adjustment of the present data.

CONCLUSIONS

Relatively straightforward Debye-Scherrer powder X-ray diffraction analyses of small samples of TiH_x - $KClO_4$ materials have contributed substantially to a large scale pyrotechnic development and production project 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. Present indications are that it will especially contribute to categories 3) and 4).

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DISCLAIMER

Identification of any commercial product does not imply recommendation or endorsement by ERDA nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

FIGURE 2 - Lattice parameter of the cubic TiH_{2-y} phase versus the overall composition of TiH_x samples.

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