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THERMAL AND ELECTROSTATIC INITIATION OF TiH_x BASED PYROTECHNICS

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ABSTRACT

The thermal and electrostatic initiations of TiH_x based pyrotechnics have been investigated to determine the material properties which influence these processes. Controlled electrostatic sensitivity experiments showed that the initiation reaction for $TiH_x/KClO_4$ pyrotechnic involved a reaction of the fuel with oxygen gas and that the $KClO_4$ chemically interacts with the titanium to desensitize the material to electrostatic ignition. Other factors which influence the initiation process were also identified. As a result of these experiments, a new theory for the electrostatic initiation of TiH_x based pyrotechnics has emerged which relates the sensitivity to ignition to the chemistry of the titanium oxides which coat the metal particles.

Thermal ignition of the $TiH_x/KClO_4$ was shown to be controlled by chemical processes associated with the titanium fuel. DTA experiments were correlated with Auger spectroscopic measurements to demonstrate the role of the dissolution of the oxide coating in the thermal ignition of titanium.

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INTRODUCTION

Although there are several models which describe the physics of ignition for pyrotechnic materials, there has been relatively little effort to determine the chemistry of initiation processes. For example, the ignition reaction for $Ti/KClO_4$ pyrotechnic compositions is generally assumed to be the pyrotechnic reaction, i.e.,

$$2Ti + KClO_4 \rightarrow 2TiO_2 + KCl.$$

While this seems to be a logical assumption, several observations related to the behavior of this material exposed to different environmental conditions raised questions that could not be adequately explained by this reaction. As a result, a number of studies were performed to resolve the chemical processes associated with the initiation of $Ti/KClO_4$ pyrotechnics. Thus far, the electrostatic and thermal initiation reactions have been studied and were shown to have some common characteristics while following different initiation mechanisms (Ref. 1-3). In this paper, the ignition data from these studies are reconciled with a proposed theory of initiation. The implications of this theory with respect to pyrotechnic material properties are also discussed with preliminary data which test behavior predicted by the theory.

EXPERIMENTAL

The instrumentation, experimental techniques, and material preparation and analyses have been previously reported in some detail (Ref. 1-3).

RESULTS AND DISCUSSION

The nominal electrostatic sensitivities of $TiH_x/KClO_4$ ($x = 0.15$, 0.65, 1.3) pyrotechnics in a fixed powder bed configuration were determined as a function of the oxygen concentration in the atmosphere surrounding the sample. The sensitivities of these powders were shown to be strongly dependent on the oxygen gas concentration at low atmospheric concentration levels while independent of oxygen concentration at high levels as shown by the curves in Figure 1. The dehydriding process used to produce the lower stoichiometry subhydrides (Ref. 4) shifts the region of oxygen dependence toward lower concentration levels. If an electrostatic insensitive material is defined as one which will not be initiated by a 20 kilovolt pulse (Ref. 5), then the minimum hydride stoichiometry acceptable for a "safe" blend can be determined from the plot of hydride stoichiometry versus percent oxygen required for initiation from a 20 KV pulse. This is done by finding the hydride stoichiometry corresponding to the natural abundance of oxygen in air as shown in Figure 2. Thus, stoichiometries of about $TiH_{0.65}$ or less should be considered to be electrostatic sensitive in air while stoichiometries above this value are considered insensitive.

Two additional observations should be noted regarding the curves in Figure 1. First, the oxygen dependence of the pyrotechnic blends shows that the electrostatic initiation reaction involves the titanium fuel with oxygen gas and is not the expected pyrotechnic reaction with $KClO_4$. Secondly, the addition of $KClO_4$ to TiH_x acts to desensitize the titanium/oxygen gas reaction to electrostatic initiation as shown by the consistently lower sensitivities of the blends as compared to titanium subhydride alone at the higher oxygen concentrations.

Numerous experiments were performed to determine the nature of the desensitizing effect produced by $KClO_4$. Figure 3 shows the relationship between blend ratio and electrostatic sensitivity for titanium ($TiH_{0.15}$) blended with $KClO_4$ as compared with Ti/Al_2O_3 mixtures. These curves show that physical dilution does not seriously affect the initiation energy for the titanium/oxygen gas reaction until the titanium/diluent ratio falls below 1/10. Thus, the desensitization must be due to a chemical mechanism. Table 1 indicates that the chemical effect is not related to a particular chemical specie. There is apparently a unique property associated with $KClO_4$ and, to a lessor extent, $KClO_3$ which produces a chemical interaction with the titanium that results in a lower sensitivity to electrostatic initiation.

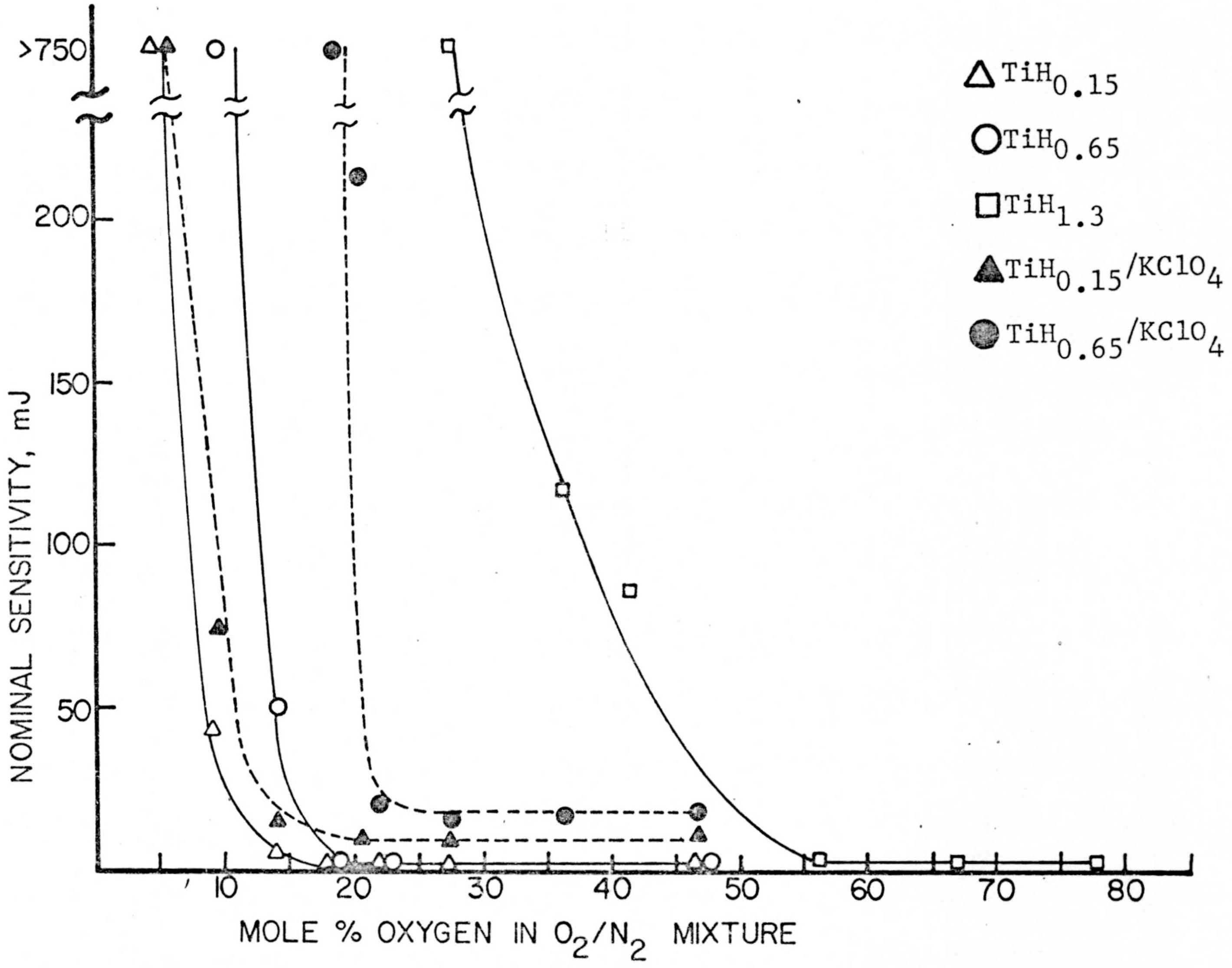

FIGURE 1. Nominal electrostatic sensitivity for TiH_x and $TiH_x/KClO_4$ blends as a function of oxygen concentration in the surrounding atmosphere.

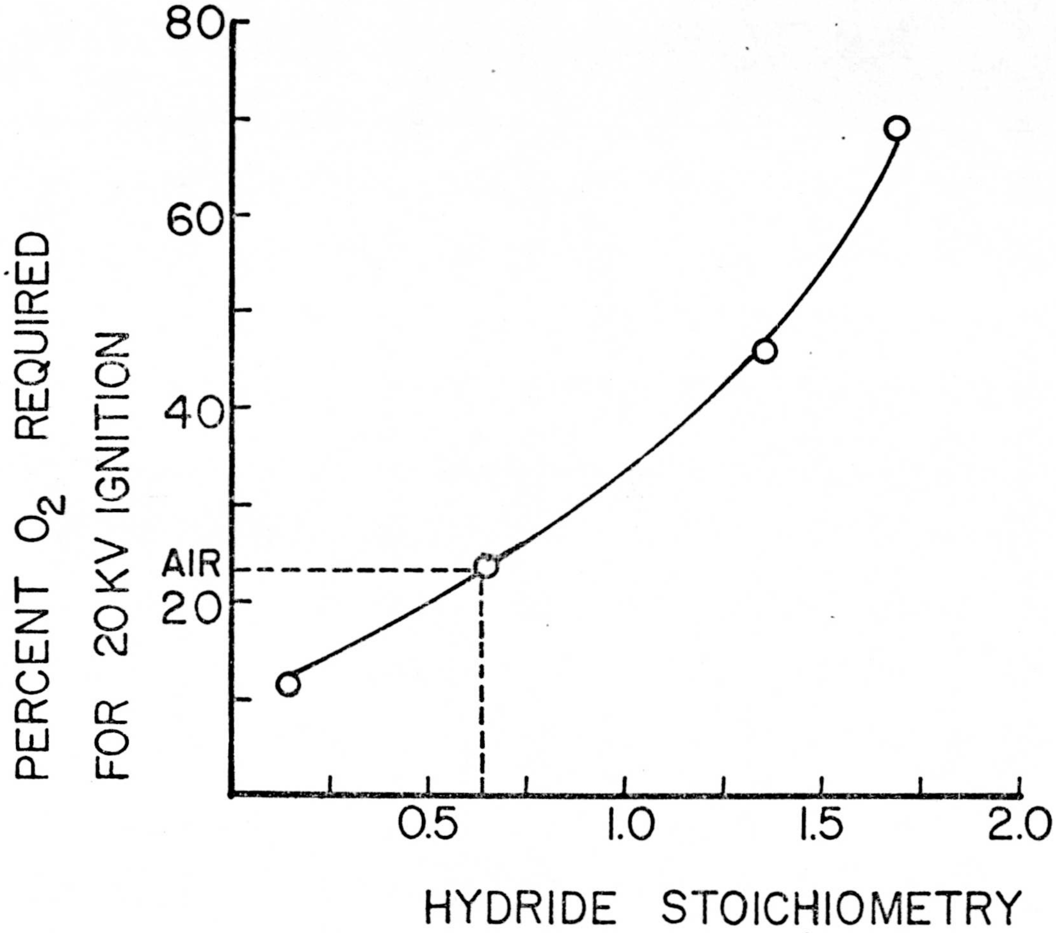

FIGURE 2. Titanium subhydride (TiH_x) stoichiometry versus oxygen concentration in surrounding atmosphere required to achieve 20kV electrostatic initiation.

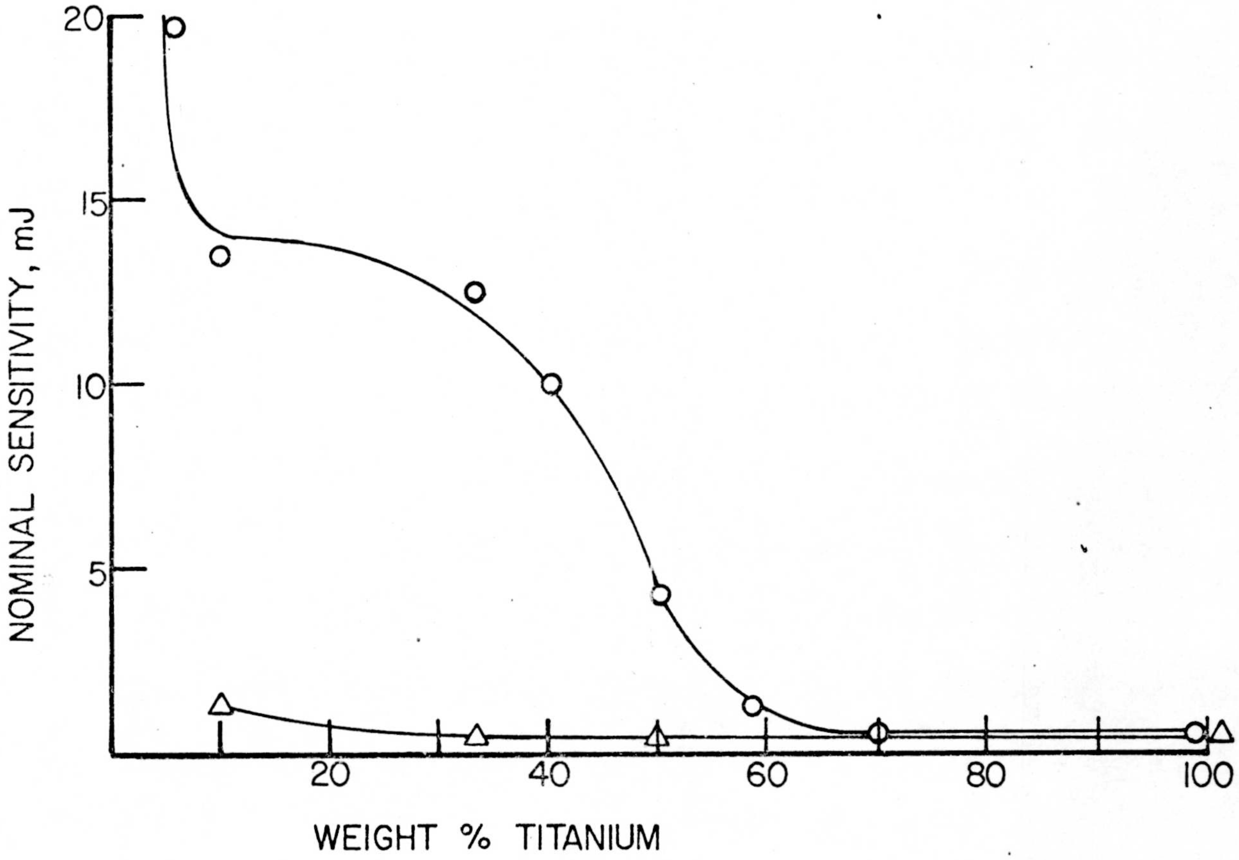

FIGURE 3. The relationship between blend ratio and the nominal electrostatic energy required for initiation of $TiH_{0.15}/KClO_4$ (○) and $TiH_{0.15}/Al_2O_3$ (△) blends in an atmosphere of 50% O_2/50% Ar.

The electrostatic initiation of TiH_x and its interactions with potassium perchlorate has been explained by considering the effects of oxides in the titanium powder. The titanium powder actually consists of titanium metal covered by an oxide coating which acts to reduce its reactivity--otherwise, the material would be pyrophoric as observed when titanium powder with a fresh metal surface is exposed to air. This oxide then controls the accessibility of the titanium to the oxidizer. Thus, we postulate that the chemistry of the material is determined by the accessibility of titanium or titanium suboxides at the surface at reactive sites or regions.

Applying the proposed model to the electrostatic initiation process, the oxygen dependence at low concentrations is due to a requirement that a minimum number of the reactive sites must have oxygen in contact for sustained combustion to occur. The curves in Figures 1 and 2 then reflect the variations in reactive site density on the surface of the particle and the oxygen concentration in the atmosphere necessary to give the minimum number of oxidation points for ignition. Titanium metal must have the maximum reactive site density on the surface and therefore requires a lower oxygen concentration in the surrounding atmosphere to achieve the minimum oxidation site requirement than the higher hydrides which must have a low reactive site density. Variations in the reactive site density with respect to hydride stoichiometry could be associated with phase changes in the material or the surface could be activated by the dehydriding process.

The potassium perchlorate would also interact with the titanium oxide surface. It has been shown that titanium oxides catalyze the thermal decomposition of $KClO_4$ (Ref. 6); this suggests that at elevated temperatures, some type of intermediate complex is formed between the $KClO_4$ and titanium oxides which provides a lower energy pathway by which the decomposition can proceed. If this interaction also occurs at lower temperatures, it could produce the desensitizing effect of $KClO_4$ on the electrostatic initiation of the titanium/oxygen reaction. Table 1 shows the number of degrees by which two catalysts lower the decomposition temperature of the oxidizers which is a measure of the effectiveness of the metal oxide as a catalyst (Ref. 6). Those

TABLE 1. Electrostatic sensitivities of titanium powder blended with various oxidizers in the ratio 33 wt % fuel/67 wt % oxidizer and tested in a 50% O_2/50% Ar atmosphere. A thermogravimetric determination of the effect of two metal oxides on the thermal decomposition temperature of the oxidizers is also shown for mixtures containing 10 mole % metal oxide/90 mole % oxidizer.

Oxidizer	Nominal Sensitivity of blend with $TiH_{0.15}$	Effect on Decomposition Temperature, ΔT_i	
		MnO_2	TiO_2
Air	<1 mJ	--	--
$KClO_4$	12 mJ	-120°	-40°
$RbClO_4$	<1 mJ	-25°	N.D.
KIO_4	<1 mJ	-10°	N.D.
$KClO_3$	4 mJ	-85°	-22°
KNO_3	<1 mJ	N.D.	N.D.

N.D. = not detectable

oxidizers that can be catalytically decomposed by the metal oxides are the same ones that exhibit the desensitizing effect.

Since titanium oxides are relatively poor catalysts for the decomposition process, a strong catalyst MnO_2, was added to the pyrotechnic mixture to determine its effect on the electrostatic sensitivity. The addition of the MnO_2 lowered the electrostatic sensitivity from 12 mJ to 2 mJ. This can be explained by considering a complex interaction between the $KClO_4$ and titanium oxides. While this complex produces a lower activation energy for the decomposition of $KClO_4$, it raises the activation energy for titanium oxides or suboxides (reactive sites) in their oxidation reactions. The addition of the strong catalyst disrupts the Ti_xO_y-$KClO_4$ complex to form the more preferred MnO_2-$KClO_4$ complex. The active Ti_xO_y regions on the surface are then free for reaction with O_2 so that the blend becomes more sensitive to electrostatic initiation.

Thermal initiation of $Ti/KClO_4$ pyrotechnics has also been studied and reported (Ref. 3 and 7). It was shown that thermal initiation was controlled by the dissolution of the oxide coating into the metal particle with the production of active titanium species on the surface. When the dissolution rate became fast enough, the heat produced by the rapid reoxidation reaction led to self-sustained reaction or ignition.

The titanium oxide coating on the particles then influences both the electrostatic and thermal initiation of titanium based pyrotechnics. However, the mechanisms for the two processes are different in enough respects to suggest that the electrostatic sensitivity might be altered without changing the thermal initiation characteristics. The objective of a "safe" hot wire initiated device then appears feasible if we assume that hot wire initiation is similar to the processes occurring in DTA type experiments.

Based upon the proposed theory, we would like to block the active sites to raise the electrostatic sensitivity without affecting the dissolution process which controls the thermal initiation. As an added benefit, blocking the active sites might also decrease the equilibrium water adsorbed by the material since it has been suggested that these sites have a high affinity for water (Ref. 1). The decreased water content should then reduce the possibility of establishing an electrochemical corrosion cell within a device which could lead to ignition failures.

A batch of $TiH_{0.65}$ was treated with carbon monoxide to determine if this molecule would attach to the reactive sites to alter the surface chemistry. The electrostatic sensitivity was decreased by about 6 kilovolts due to this treatment. The moisture level for the treated material was 0.05 wt % which is below background for the untreated material.

Since the reactive regions seem to be associated with titanium suboxides, some $TiH_{0.15}$ powder was heated to 300°C in oxygen and held isothermally for a period to determine if the surface could be more fully oxidized. This treatment resulted in a decrease of about 5 kilovolts in the electrostatic sensitivity and a change in moisture content from 0.82 to 0.57 wt %. Moisture levels were determined after exposing the material to 60% RH at 22°C for five days. Thus, the preliminary data suggests that alterations in the surface chemistry can alter the electrostatic initiation and water adsorption properties of the material. DTA ignition was unchanged by the treatment.

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