

SURFACE COMPATIBILITY STUDIES OF POTASSIUM PERCHLORATE REACTION WITH PYROTECHNIC FUELS

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ABSTRACT

Surface sensitive x-ray photoelectron spectroscopy (XPS) and x-ray induced Auger electron spectroscopy (XAES) were used to analyze surface changes in Fe/KClO₄, TiH_{0.65}/KClO₄ and Al foils in KClO₄ during accelerated aging at 60 and 120°C. The result shows a 0.02% Cl⁻ formation per day in Fe/KClO₄ and TiH_{0.65}/KClO₄ powders aged at 120°C for ≤145 days. No KClO₄ decomposition was observed under the similar aging conditions in KClO₄ samples without pyrotechnic fuels. Titanium oxide to KClO₄ signal ratio in a pressed disk of TiH_{0.65}/KClO₄ was found to be lower than that of the powdered samples. Carbon impurities were noted in all powders, especially strong in metal (or subhydride) containing specimens; carbon impurities were slightly removed from the subhydride during aging.

INTRODUCTION

The chemical reaction mechanism of solid mixtures of pyrotechnic materials is very complex. It may consist of several elementary processes involving changes in the particle structure, physical state, and chemical composition of each reactant. Particle surface films and their chemical compositions are critical factors that determine the property of the contact surface through which chemical reaction would occur. Consequently, understanding pyrotechnic material compatibility requires understanding the deviations in surface compositions that can occur in both fuel and oxidizer during storage.

To enhance our quality control in energetic material production at Mound, we have investigated the surface compositions and their changes in thermites, pyrotechnics, and plastic bonded explosives (PBX) by spectroscopic approaches (ref.1-13). In Al/Cu₂O thermite, a thin film of Al₂O₃ was observed on the fuel surface by x-ray photoelectron spectroscopy and x-ray induced Auger electron spectroscopy. The thickness of this oxide film was found to increase during mixing with the oxidizer, accelerated aging, and pelletizing at elevated temperature. However, under specific aging and pelletizing conditions there is

*Mound is operated by Monsanto Research Corporation for the U.S. Department of Energy under Contract No. DE-AC04-76DP00053.

a limit to oxide-growth; the aluminum fuel appears to be well protected by the oxide layer at its maximum thickness, and the thermite remains compatible (ref.1,2). A very similar phenomenon was also observed for Al/Fe₃O₄ thermite, except the aluminum oxide film was slightly thicker than that of Al/Cu₂O (ref.3,4).

To investigate the reaction mechanism for a pyrotechnic system, one has to understand the preignition state of fuel-oxidizer interface. With scanning Auger microscopy (SAM), we have observed the formation of "mixed zones" in the pelletized thermite systems of Al/Cu₂O, Al/Fe₂O₃, Al(Si)/Fe₂O₃ and Al/Fe₃O₄. These mixed zones are responsible for the ignition initiation of these systems and support our differential scanning calorimetry (DSC) results that show the ignition temperature in pellets to be substantially lower than those in the powders where the mixed zones are not readily formed (ref.5-8). In the case of the titanium-based pyrotechnics, the mechanism involves first the dissociation of surface oxide film and then diffusion of oxygen into the fuel so that a metallic surface is formed for reaction with oxidizer (ref. 9). It was shown that the rate of oxygen dissolution increased sharply at ~350°C in titanium but ~500°C in titanium subhydrides (ref.9,10). The outward diffusion of hydrogen in subhydrides that inhibits the inward diffusion of oxygen attributes to the delay of oxygen diffusion. By Fick's Second Diffusion Law, the activation energy of oxygen diffusion in titanium was calculated to be 28 kcal/mole (ref. 11,12).

Potassium perchlorate (KClO₄) is one of the most commonly used oxidizers in the pyrotechnic blends manufactured by Mound and some other weapon laboratories. Consequently, the stability of potassium perchlorate, with or without additives, is of great importance to the compatibility of the pyrotechnic products and related components. Thermal decomposition of KClO₄ can generally be divided into two stages: a relatively slow reaction corresponding to the initiation of the decomposition, and then a much faster propagation by a chain-branching mechanism resulting from the difference between the rate of activating an oxygen rich group and the rate of atomic oxygen transport from this oxygen rich group to its oxygen deficient neighbors (ref.14). The presence of the solid reaction products, chlorides, plays an important role to the autocatalytic decomposition of KClO₄ (ref.15). The presence of metal oxides, such as Fe₂O₃ or TiO₂ from the fuel surface film of pyrotechnic materials, would also enhance the catalytic decomposition of KClO₄; this can be interpreted by the mechanism of electron transfer from the perchlorate ions to positive holes in the oxides (ref.16). Finally, the effect of residual carbon from the powder surface to the stability of KClO₄ should not be ignored (ref.17).

In this paper, we will present mainly the surface compatibility results of KClO₄ in pyrotechnic materials of Fe/KClO₄, TiH_{0.65}/KClO₄ and Al foils in KClO₄, during accelerated aging at 60 and 120°C investigated by x-ray

photoelectron spectroscopy and x-ray induced Auger electron spectroscopy. The metal (or subhydride), oxide, carbon and oxygen results will also be discussed.

EXPERIMENTAL

$TiH_{0.65}$ powders were prepared at Mound by passing hydrogen gas through Ti powders at high temperature and then cooling down to lower temperature to form TiH_x of desired x value ($0.65 \leq x \leq 2.0$). $TiH_{0.65}/KClO_4$ was blended at Mound (PA-38, 33.0/67.0 weight ratio). $Fe/KClO_4$ was also blended at Mound (FEK-002, 84/16 weight ratio). In this case of $Al/KClO_4$ study, aluminum foil strips were aged with $KClO_4$ powders. Each sample was aged in a glass vial opened to air, and then pulled out for XPS and XAES analyses at different times. The aging temperatures were 60 and 120°C.

An aged specimen was lightly sprinkled on one side of a double-sided sticking tape and affixed to a copper sample holder. It was then placed in a high vacuum preparation chamber of less than 10^{-7} torr for about 1 hr, then directly, without exposure to air, transferred to an ultra high vacuum analysis chamber ($<10^{-9}$ torr). The analysis chamber is part of a Kratos X-SAM 800 instrument which allows XPS and XAES studies to be performed. For these examinations, Mg $K\alpha$ x-ray radiation of 1253.6 eV was used. This radiation was excited by using an anode potential of 7.5 kV and 2 mA of current. This anode potential holds Bremsstrahlung radiation to a minimum but has sufficient potential to excite the Mg $K\alpha$ characteristic line. Bremsstrahlung radiation is known to cause decomposition of $KClO_4$ (ref.18).

The Cl 2p, O 1s, C 1s, and K 2p photopeaks were examined for each sample containing $KClO_4$. Chemical shifts in the Cl 2p and O 1s data were measured relative to C 1s and K 2p photolines. Three chlorine photopeaks are known to be observable in the Cl 2p spectrum; they are from ClO_4^- , ClO_3^- and Cl^- species. The difference in kinetic energy between the Cl 2p peaks of the ClO_3^- and Cl^- relative to the ClO_4^- were measured to be 2.2 eV and 10.4 eV, respectively. The intensities of the three peaks were monitored as a function of aging. Data for each sample were recorded within a period of 1 hr; no detectable ClO_3^- and Cl^- formation could be noted due to the x-ray decomposition, such as photo-decomposition of perchlorate by Bremsstrahlung radiation.

RESULTS AND DISCUSSION

Oxidizer surface decomposition

To investigate the surface stability of $KClO_4$ during aging at 60 and 120°C, with or without the presence of pyrotechnic fuels, is the main interest of this study. Fig. 1 illustrates the Cl 2p XPS spectra of (a) unaged $KClO_4$ with no detectable ClO_3^- or Cl^- , (b) artificially decomposed $KClO_4$ with detectable amounts of ClO_3^- and Cl^- , and (c) the difference between the artificially

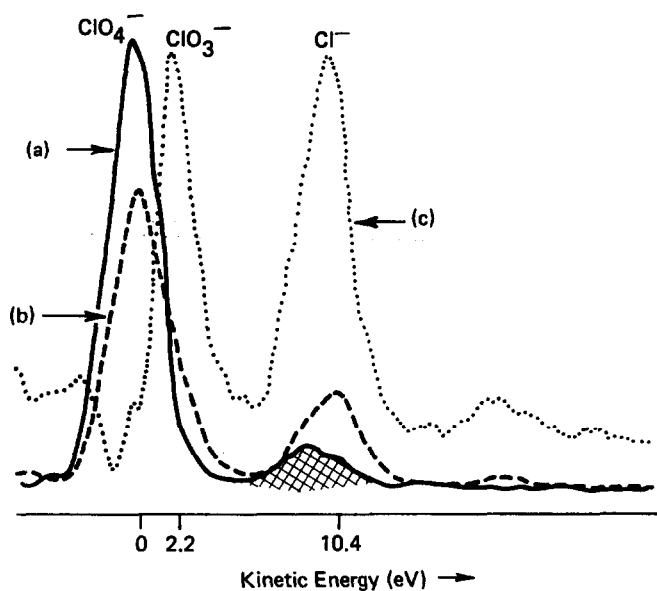


Fig. 1. Cl 2p XPS photoelectron signals of ClO_4^- , ClO_3^- , and Cl^- from (a) an unaged KClO_4 sample, (b) a decomposed KClO_4 sample, and (c) difference spectrum of (a) and (b) enlarged by factor 5.

decomposed and the unaged. Note that the sensitivity in (c) is 5 times that of (a) and (b). The peak appearing at zero relative kinetic energy (binding energy 208 eV) for unaged KClO_4 is due to Cl 2p photoionization by Mg $\text{K}\alpha_{1,2}$ radiation, which is a barely resolvable doublet of $2P_{1/2}$ and $2P_{3/2}$ spin-orbit splitting; and the broad peak appearing at 8.5 eV relative kinetic energy (cross-hatched area) is due to Cl 2p photoionization by Mg $\text{K}\alpha_{3,4}$ satellite radiation created in the Mg anode. The artificially decomposed KClO_4 spectrum (Fig. 1b) was created by irradiating the non-monochromatized Mg $\text{K}\alpha$ x-rays for longer than 50 hr; these x-rays are known to contain Bremsstrahlung radiation which leads to perchlorate decomposition (ref.19). The amount of ClO_3^- and Cl^- produced by decomposition can be calculated from the difference spectrum of Fig. 1c. One can immediately note that the resulting ClO_3^- peak has been chopped off on the low kinetic energy side of the peak; thus increasing the uncertainty in the determination of the chlorate intensity. Errors developed in measuring the ClO_3^- intensity do not exceed $\pm 10\%$ of the signal; Cl^- determinations result in significantly less error at $\pm 2\%$. The error developed in determining the intensity is directly related to the total counts (N), including background, in the peak. Usually, 1 hr is spent measuring the XPS Cl 2p spectrum; this is to ensure that no detectable ClO_3^- or Cl^- is produced due to x-radiation damage.

Increased counting times would correspondingly decrease the error in the intensity measurements by $\pm \sqrt{N_p + N_b}$, where N_p and N_b are the counts in the peak and background, respectively.

Perchlorate decomposition into ClO_3^- and Cl^- due to thermal aging was measured via difference spectra, very similar to Fig. 1c. Fig. 2 shows the difference spectrum between two thermally aged Fe/ KClO_4 powdered specimens at 120°C , spectrum for a sample aged for 145 days subtracted from that of a 10 day sample. Note that positive peaks at ClO_3^- and Cl^- energy positions indicate the increase in both the ClO_3^- and Cl^- signals as aging time increases. Results of thermal aging decomposition of KClO_4 with or without pyrotechnic fuels are tabulated in Table 1. From this table, one can see it is very difficult to draw any conclusion about chlorate formation mainly because of the relatively large uncertainty introduced from the spectrum analysis. However, Cl^- concentrations due to thermal aging can be plotted and are shown in Fig. 3. The computer best-fit chloride growth rates on particle surfaces of Fe/ KClO_4 and $\text{TiH}_{0.65}/\text{KClO}_4$ were also shown in Fig. 3. It appears that the growth rates are approximately equal for these two pyrotechnic blends aged at 120°C . The rates are both 0.02% per day. It is obvious from this figure that the initial Cl^- concentration is higher in Fe/ KClO_4 than $\text{TiH}_{0.65}/\text{KClO}_4$, possibly because of surface reaction during blending. No Cl^- growth was detected in KClO_4 powders aged without fuel at 120°C . This suggests that at 120°C the KClO_4 decompositions in the pyrotechnic materials were induced by the surface contact with fuels. In the case of Al aged in KClO_4 , the KClO_4 sampled is most likely not the powders in contact with Al foils. This explains why no Cl^- formation was observed in these samples.

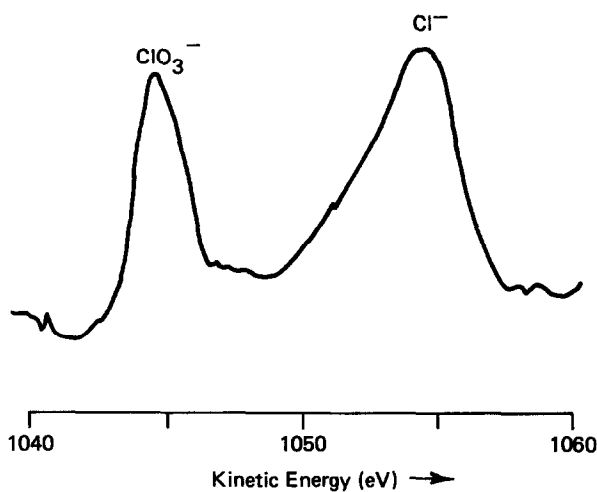


Fig. 2. Cl 2p XPS difference spectrum of two Fe/ KClO_4 samples aged for 145 days and 10 days at 120°C .

TABLE 1

Surface decomposition of KClO_4 due to thermal aging at 60 and 120°C as detected by x-ray photoelectron spectroscopy.

Run No.	Sample	Aging Conditions	Cl 2p Intensity (%)		
			ClO_4^-	ClO_3^-	Cl^-
A080	KClO_4	42 days at 60°C	99	a	a
A010	KClO_4	145 days at 60°C	99	a	a
A060	KClO_4	42 days at 120°C	99	a	a
A030	KClO_4	145 days at 120°C	99	a	a
A110	$\text{TiH}_{0.65}/\text{KClO}_4$	Room temperature storage	97	<0.9	<2.0
A240	$\text{TiH}_{0.65}/\text{KClO}_4$	10 days at 60°C	98	b	2.0
A230	$\text{TiH}_{0.65}/\text{KClO}_4$	22 days at 60°C	97	b	3.0
A220	$\text{TiH}_{0.65}/\text{KClO}_4$	42 days at 60°C	97	b	2.5
A140	$\text{TiH}_{0.65}/\text{KClO}_4$	145 days at 60°C	98	b	2.0
A170	$\text{TiH}_{0.65}/\text{KClO}_4$	22 days at 120°C	96	2.0	2.0
A160	$\text{TiH}_{0.65}/\text{KClO}_4$	42 days at 120°C	97	b	3.0
A120	$\text{TiH}_{0.65}/\text{KClO}_4$	145 days at 120°C	91	4.5	4.5
P090	Fe/KClO_4	10 days at 60°C	96	b	4.0
P070	Fe/KClO_4	22 days at 60°C	98	b	2.0
P020	Fe/KClO_4	145 days at 60°C	97	b	3.0
P050	Fe/KClO_4	10 days at 120°C	94	b	5.4
P060	Fe/KClO_4	22 days at 120°C	94	b	6.0
P040	Fe/KClO_4	42 days at 120°C	93	b	7.0
P030	Fe/KClO_4	145 days at 120°C	91	b	9.0

^aAll less than 0.6 for ClO_3^- of Cl^- , no detectable aging effect.

^bNo determination made.

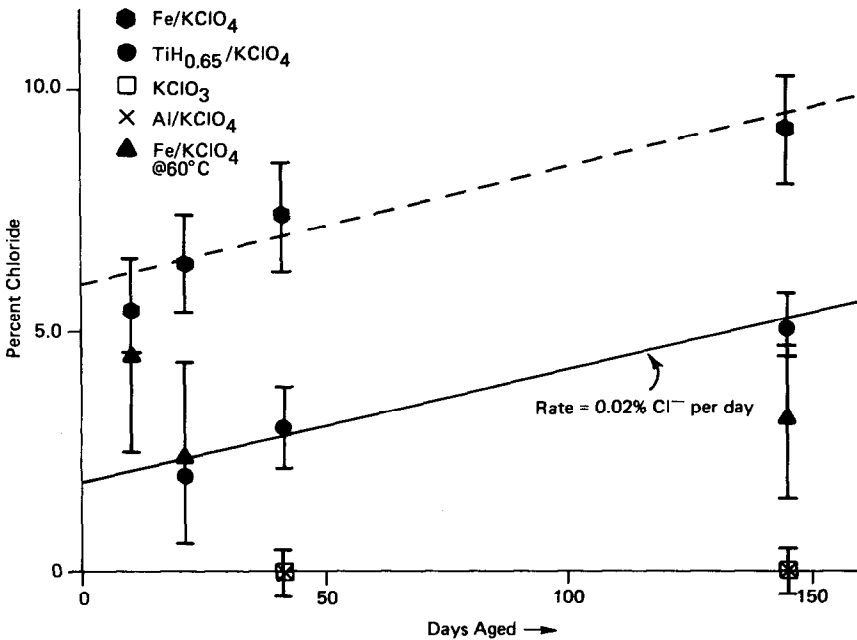


Fig. 3. Chloride concentrations on pyrotechnic material powder surfaces during aging at 120°C.

Fuel surface analyses

Aluminum surface oxide. Fig. 4 shows Al KLL Auger electron lines induced by x-radiation from (a) unaged Al foil and (b) Al foil aged with KClO_4 at 120°C for 145 days. The main peaks at the lower kinetic energy are due to XAES electrons from Al_2O_3 surface films. The peaks at higher kinetic energy are due

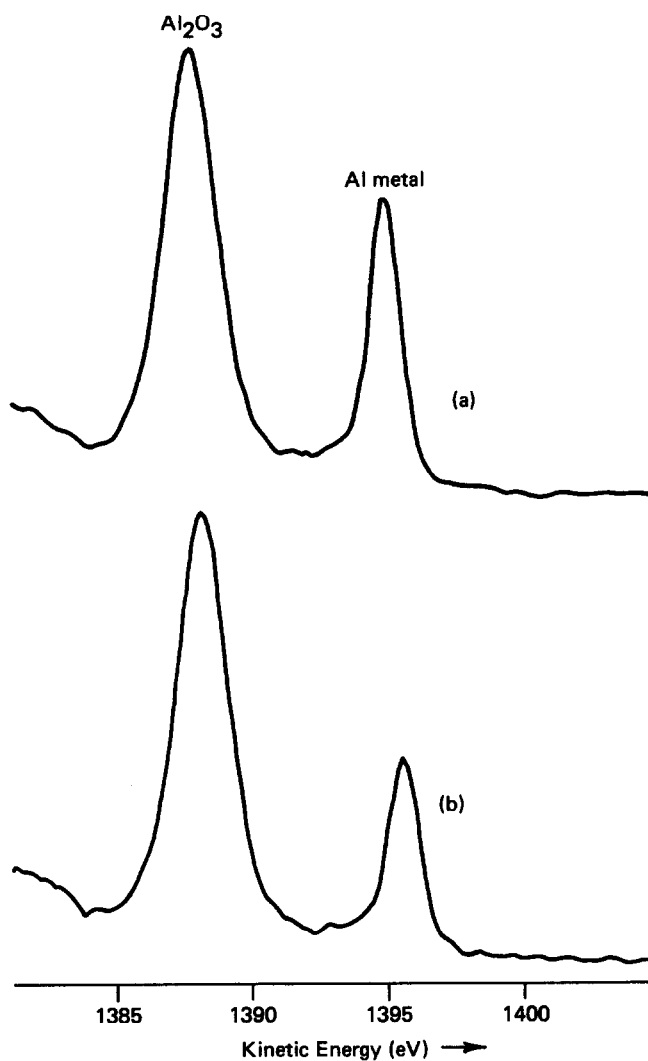


Fig. 4. Al KLL x-ray induced Auger electron lines of Al foils (a) unaged, (b) aged for 145 days with KClO_4 at 120°C .

to Al metal. One can see easily that the oxide layer is thinner on the unaged Al foil than in the sample aged with $KClO_4$. The oxide film thickness, d_o , can be calculated from the equation

$$d_o = \lambda_o \ln[(I_o/I_m)(I_m^\infty/I_o^\infty) + 1] \quad (1)$$

where λ_o is the mean free path of an Al_2O_3 electron; I_o and I_m are measured spectroscopic signal intensities for Al_2O_3 and Al metal, respectively; I_o^∞ and I_m^∞ are intensities for "infinitely" thick samples of such materials. The details of this relation have been published previously (ref.1,2).

Taking 0.7514 for (I_m^∞/I_o^∞) from our previous work and 16.6 Å for λ_o (ref.20), we obtain the oxide film thicknesses of 17.5 Å and 21.2 Å for an unaged Al foil and one aged with $KClO_4$ for 145 days at 120°C, respectively. These results, along with others, are listed in Table 2. From these results, we can conclude that a) no detectable oxide growth has been observed in Al foils aged at 60°C, 100°C, and 120°C with $KClO_4$ up to 145 days; and b) an increase of 2 ~ 3 Å oxide film thickness on Al surfaces was caused by contact with $KClO_4$.

TABLE 2

Al_2O_3 film thicknesses on Al aged with $KClO_4$ as calculated from Al KLL Auger signals

<u>Sample and aging conditions</u>	<u>Oxide film thickness (Å)</u>
Al foil alone, unaged	17.5
Al in $KClO_4$, 10 days at 60°C	20.4
Al in $KClO_4$, 22 days at 60°C	20.4
Al in $KClO_4$, 42 days at 60°C	21.0
Al in $KClO_4$, 10 days at 100°C	20.4
Al in $KClO_4$, 22 days at 100°C	20.7
Al in $KClO_4$, 42 days at 100°C	19.7
Al in $KClO_4$, 10 days at 120°C	21.0
Al in $KClO_4$, 22 days at 120°C	21.4
Al in $KClO_4$, 42 days at 120°C	21.4
Al in $KClO_4$, 145 days at 120°C	21.2

Titanium and Iron XPS Analyses. Very thick oxide layers have been observed from our Ti, TiH_x , and Fe pyrotechnic fuels; only limited success has been accomplished to penetrate through the thick oxides and detect the metal or sub-hydrides (ref.21). Fig. 5 shows Ti 2p XPS signals from powdered samples of (a) $TiH_{0.65}$ unaged powders, (b) unaged $TiH_{0.65}/KClO_4$, (c) $TiH_{0.65}/KClO_4$ aged 145 days at 120°C, and (d) TiO_2 . The main peaks at kinetic energy ~794 eV are due to Ti $2p_{3/2}$ from TiO_2 . Consequently, all powders were found to have very thick oxides. However, a very weak metal (or hydride) signal was

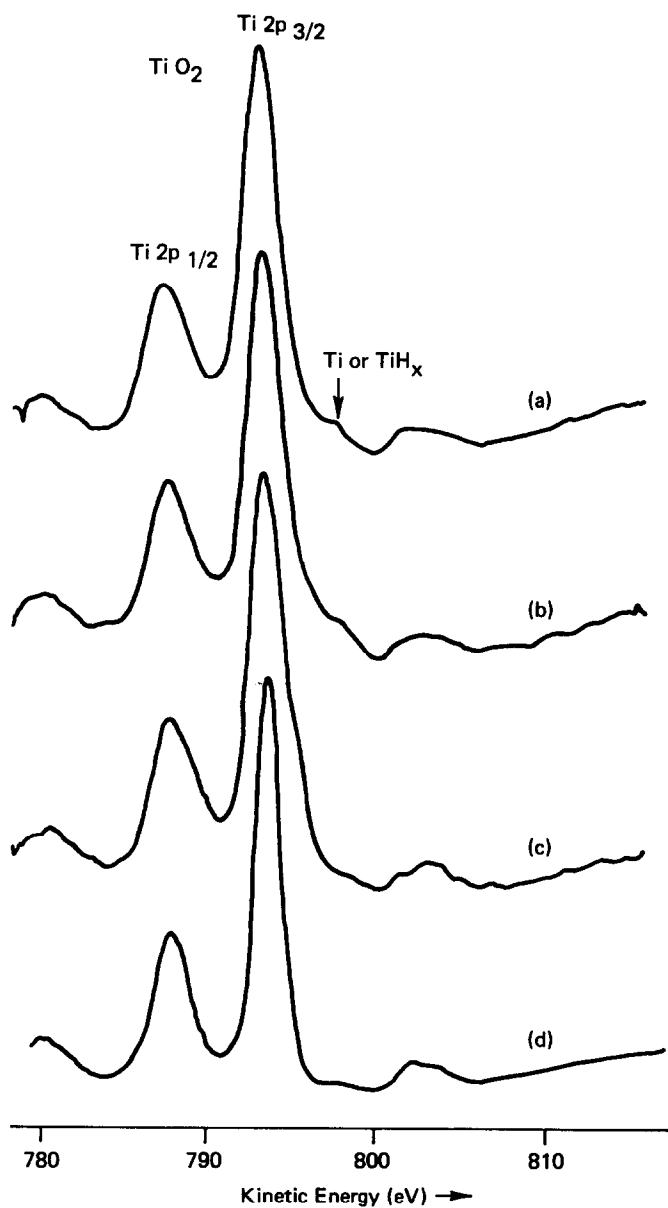


Fig. 5. Ti 2p XPS photolines of (a) $\text{TiH}_{0.65}$, (b) unaged $\text{TiH}_{0.65}/\text{KClO}_4$, (c) $\text{TiH}_{0.65}/\text{KClO}_4$, 145 days at 120°C , and (d) TiO_2 .

detected 4.4 eV higher in kinetic energy from the main peaks in Fig. 5a and 5b. Disappearance of this weak signal after aging at 120°C for 145 days (Fig. 5c) indicates thermal induced oxidation occurred during aging. It is interesting to compare the linewidth of the TiO_2 sample (Fig 5d) to those from $\text{TiH}_{0.65}$ or its blend. The linewidth from TiO_2 sample at half maximum intensity is 1.9 eV, while from $\text{TiH}_{0.65}$ is 2.5 eV. This 0.6 eV line-broadening in $\text{TiH}_{0.65}$ can be interpreted as the suboxides, which are only 1 to 3 eV away from TiO_2 signal, on the surface of subhydride powders (ref.22).

The iron oxide layer on iron is so thick in Fe/KClO_4 blend (either before or after aging), as can be seen from Fig. 6, that no effect caused by aging can be detected on iron metal surfaces.

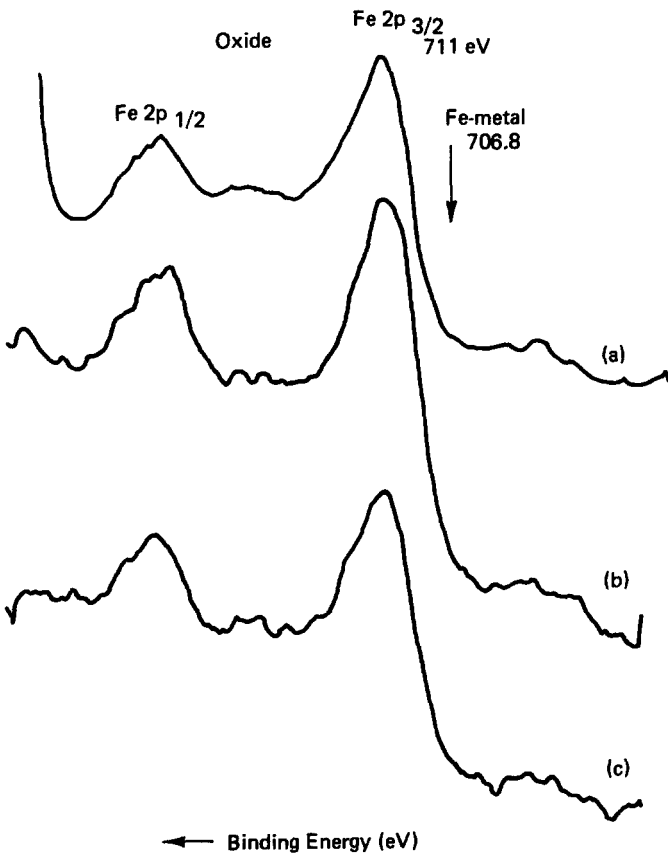


Fig. 6. Fe 2p XPS signals of (a) Fe_2O_3 , (b) unaged Fe/KClO_4 , and (c) Fe/KClO_4 , 145 days at 120°C.

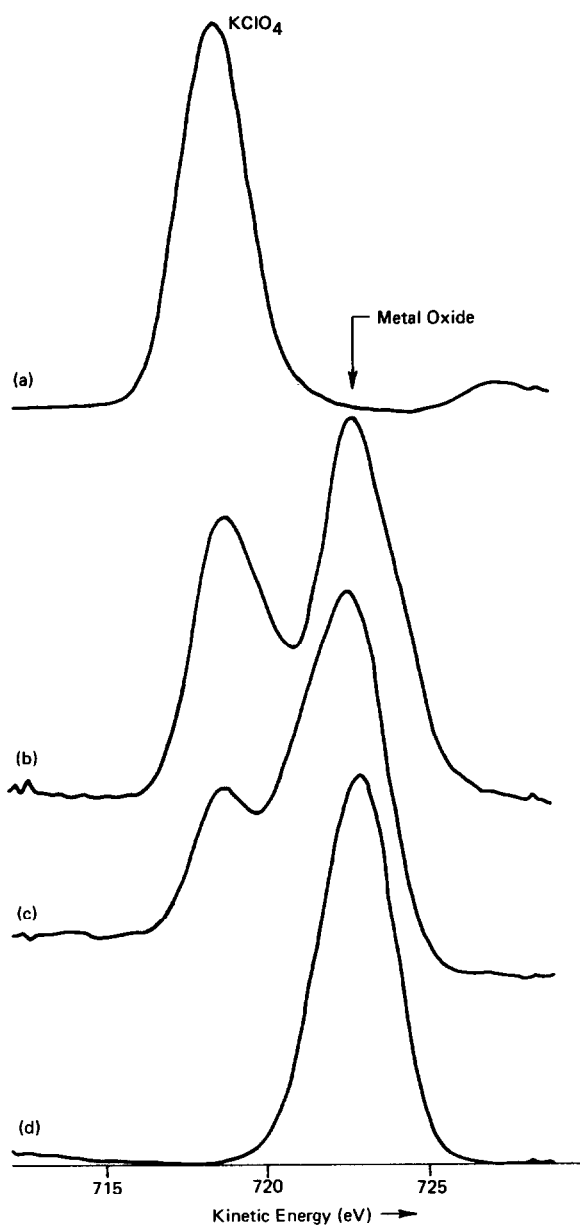


Fig. 7. 0 1s XPS photolines for (a) KClO₄, (b) TiH_{0.65}/KClO₄, (c) Fe/KClO₄, and (d) Al in KClO₄; all samples have been aged for 145 days at 120°C.

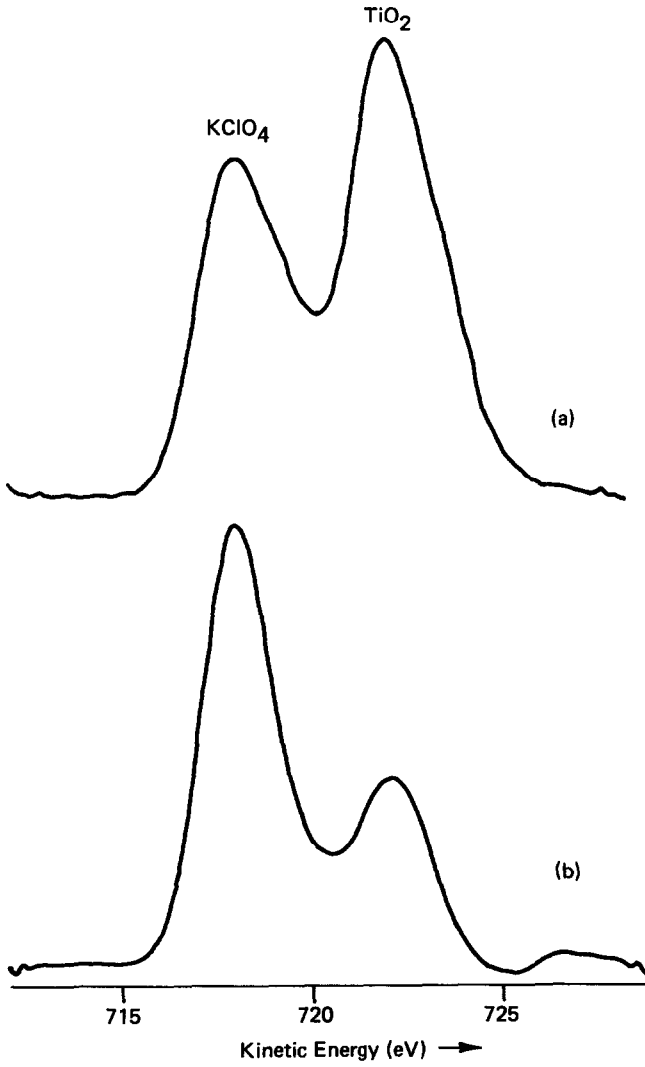


Fig. 8. 0 1s XPS comparison of surface compositions of $\text{TiH}_{0.65}/\text{KClO}_4$ (a) powders, (b) pressed disk form.

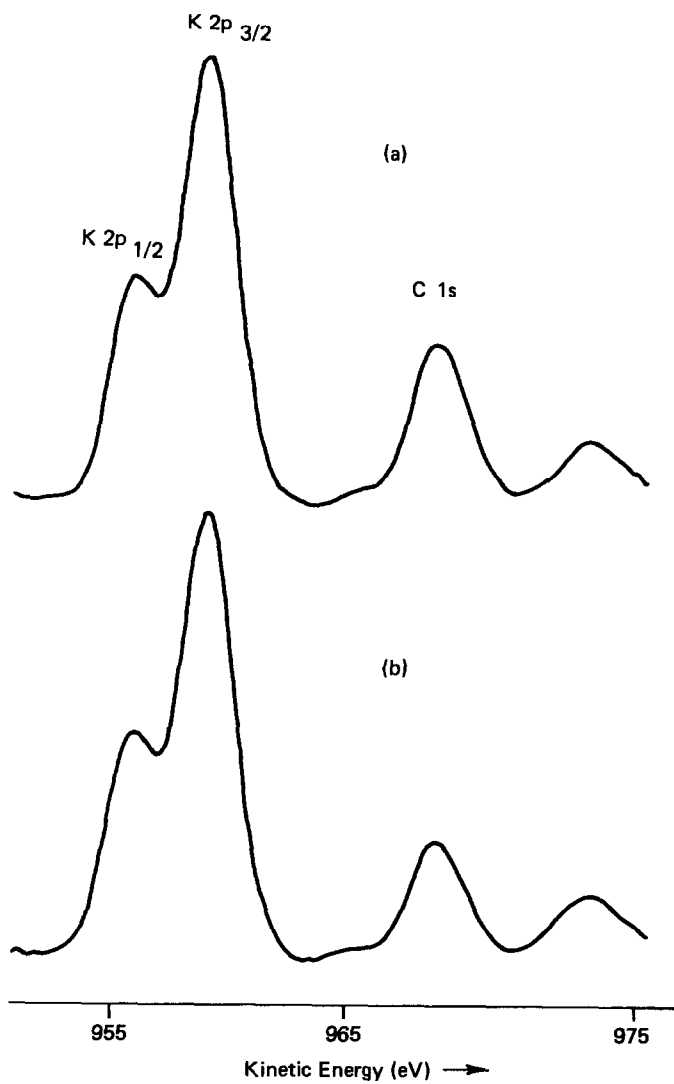


Fig. 9. K 2p and C 1s XPS signals of (a) unaged KClO_4 , and (b) KClO_4 , aged 145 days at 120°C .

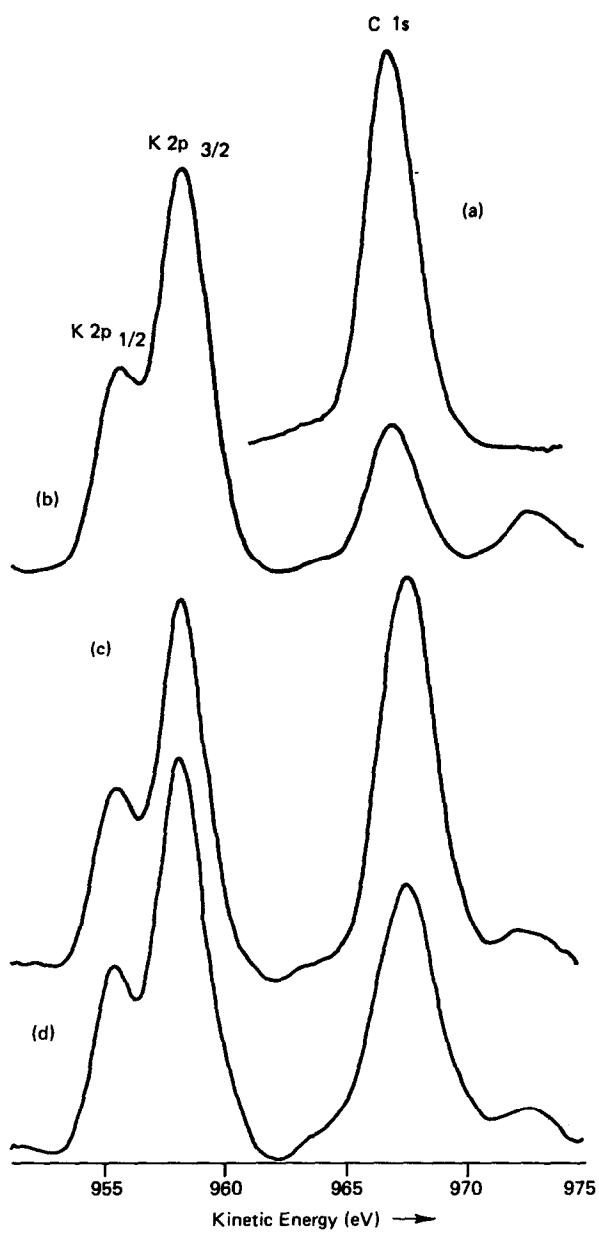


Fig. 10. K 2p and C 1s XPS signals of (a) $\text{TiH}_{0.65}$, (b) KClO_4 , (c) unaged $\text{TiH}_{0.65}/\text{KClO}_4$, (d) $\text{TiH}_{0.65}/\text{KClO}_4$ aged for 10 days at 120°C .

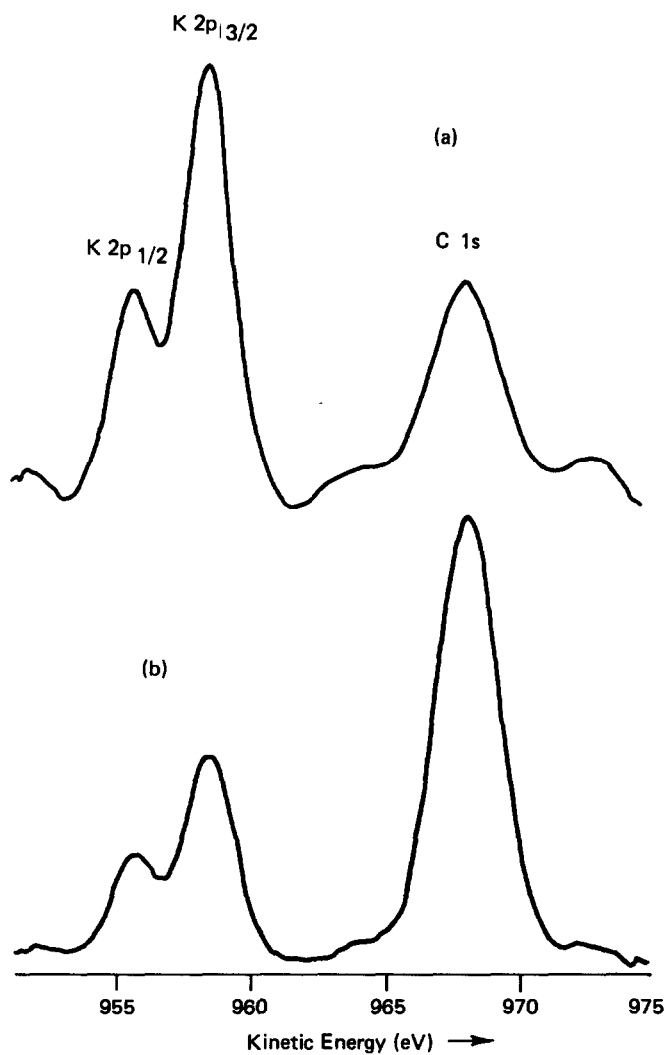


Fig. 11. K 2p and C 1s XPS spectra of (a) unaged Fe/KClO₄, and (b) Fe/KClO₄ aged 145 days at 120°C.

Oxygen 1s, carbon 1s and potassium 2p XPS signals

Fig. 7 shows O 1s XPS photolines of (a) $KClO_4$, (b) $TiH_{0.65}/KClO_4$, (c) $Fe/KClO_4$ and (d) Al aged with $KClO_4$. All samples were aged at 120°C for 145 days. The peaks at kinetic energy near 719 eV are from the oxygen of $KClO_4$ and those near 723 eV are from oxygen of metal oxides. Note that the linewidth of iron oxide (3.5 eV) is considerably larger than that of Al_2O_3 (2.7 eV) or TiO_2 (2.9 eV). This may suggest that a slight corrosion due to H_2O occurred on Fe surfaces. Another interesting result is that the O 1s intensity ratio of $KClO_4$ to TiO_2 in $TiH_{0.65}/KClO_4$ powders was found to be smaller than that of a pressed disk (Fig. 8). This may indicate the crushing of TiO_2 surface film on $TiH_{0.65}$ during disk-pressing, or even redistribution of disk surface components in favor of $KClO_4$.

All powder surfaces will have residual carbon impurities as can be observed from C 1s XPS. This residual carbon was slightly removed from $KClO_4$ or $TiH_{0.65}/KClO_4$ after thermal aging (Fig. 9 and 10). But, this is not the case in $Fe/KClO_4$. Fig. 11 shows, in contrast, an increase in carbon during aging $Fe/KClO_4$, possibly due to corrosive nature of Fe surfaces. A stronger C 1s signal with specimens that contain fuel was also observed. This is due to either stronger adsorption of hydrocarbon on metals or photon/photoelectron induced adsorption on the metal surfaces.

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