

OXIDATION OF TANTALUM METAL BY LEAD PEROXIDE AND RED LEAD

S. R. YOGANARASIMHAN*, N. S. BANKAR, S. B. KULKARNI**
and R. G. SARAWADEKAR

*Explosives Research and Development Laboratory, Armament Post, Pashan,
Pune-411 021, India*

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The kinetics of oxidation of metallic fuels by metal oxides involve some of the most important parameters determining the utility of any metal oxide system in pyrotechnic applications. An attempt has been made to study the oxidation of Ta metal by strong oxidizers such as PbO_2 and Pb_3O_4 , employing differential thermal analysis and infrared spectroscopy. The rate of oxidation of Ta increases with increasing oxidizer content in both Ta– PbO_2 and Ta– Pb_3O_4 , systems. A tentative mechanism for the observed phenomenon is proposed.

A metal oxidant composition is used as the main part of a pyrotechnic delay column in fuses. The delays required in the fuses may range from a few seconds to a few milliseconds. The kinetics of oxidation of the metal fuel, which are determined predominantly by the oxidizer employed, control the delay timings. Though any metal – oxidizer system is potentially an effective delay composition, metals such as Si, Zr, Ni, Mo, Ti, B and W in conjunction with oxidizers such as chromate, chlorate, nitrate, perchlorate, Fe_2O_3 and Pb_3O_4 have been suggested for use. Many of the above metals yield oxides of varying stoichiometry and the kinetics will therefore be highly susceptible to changes in the oxidizer and the oxidizer content. Hogan and Gordan [1] were among the first to apply thermal methods to a systematic study of a pyrotechnic delay system. Charsley *et al.* [2, 3] have described the kinetics of oxidation of B and W by oxidizers such as $\text{K}_2\text{Cr}_2\text{O}_7$ and MoO_3 , employing thermal analysis and temperature profile measurements Nagaishi *et al.* [4] found during their studies on the combustion of W by KClO_4 in the presence of an auxiliary oxidizer BaCrO_4 that different conditions of energy supply can cause apparent inconsistencies in the ignition time recorded in the different thermal methods.

Ta on the other hand always yields Ta_2O_5 in an oxidizing atmosphere, the oxidation reaction being reported to be highly exothermic. Since no information is available in the literature on the system Ta + strong oxidizers, we have investigated the systems Ta + PbO_2 and Ta + Pb_3O_4 , employing DTA and infrared spectroscopy, the results of which are described in this communication.

* To whom all correspondence should be addressed.

** Present address: Hindustan Lever, R and D Section, Bombay.

Experimental

Materials

The Ta metal powder had an average particle size of 10.5μ . The surface area was found to be $5710 \text{ cm}^2/\text{cm}^3$. The lead peroxide and red lead had particle sizes and surface areas of 4.0μ , $15000 \text{ cm}^2/\text{cm}^3$ and 6.0μ , $10000 \text{ cm}^2/\text{cm}^3$, respectively. These correspond to approximately $3000 \text{ cm}^2/\text{g}$ and $2000 \text{ cm}^2/\text{g}$, respectively.

Since these mixtures are highly pyrophoric, adequate safety precautions were taken during mixing, which was usually carried out by sieving the ingredients together in appropriate sieves behind safety screens.

Measurements

DTA was carried out in a unit designed and fabricated in our laboratory. It consisted of Stanton Redcraft linear variable rate temperature programmer, which can give rates of heating from $2^\circ/\text{min}$ to $20^\circ/\text{min}$. The samples were housed in platinum thermocups to the bottom of which Pt/Pt-Rh 13% thermocouples were fused. The temperatures and differential temperatures were recorded on a Digilog twin-channel strip chart recorder with a sensitivity of $5 \mu\text{v}$. Alumina was used as reference material.

Accurately weighed (approx. 10 mg) samples were taken in the sample cup and an equal mass of the inert reference material, alumina, was in the reference cup. Differential thermal analysis profiles were obtained for the Ta-PbO₂ and Ta-Pb₃O₄ systems at different compositions, i.e. w/w ratios of 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0. The rate of heating was $15^\circ/\text{min}$ for all compositions.

Infrared spectra of the final products were recorded on a Perkin-Elmer IR spectrophotometer model No. 457 in 0.5% KBr pellets.

Results and discussion

Figure 1 shows the differential thermal analysis profile of PbO₂. The first endothermic reaction starts at 364° , giving a broad and shallow peak at 417° . The second endotherm has a peak temperature of 451° . The inception of the third endotherm is at 563° and it reaches a maximum at 601° . The inception and peak temperatures of all the endotherms during the decomposition of PbO₂, and the

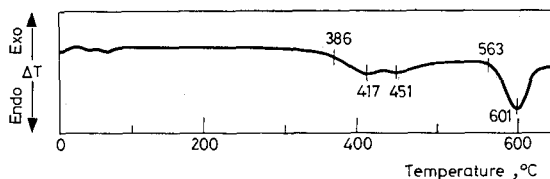
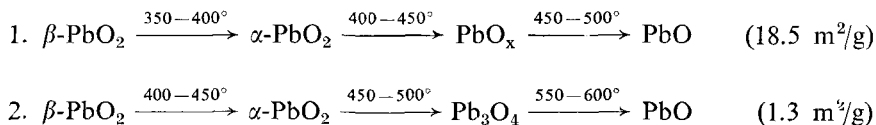


Fig. 1. DTA of PbO₂

stoichiometries of the decomposition products, have been variedly reported. Fouque *et al.* [5] could correlate such differences with the surface areas of the PbO_2 samples in the course of their studies on the thermal analysis of PbO_2 . They proposed a surface mechanism for the thermal decomposition of $\beta\text{-PbO}_2$ as follows:



The temperatures of the $\beta - \alpha$ inversion and the subsequent decomposition vary over a range of about 50° , depending on the surface area, higher surface areas having the effect of lowering the temperatures. The peak and inception temperatures recorded in our DTA of PbO_2 correspond very closely with the scheme for reactions proposed for the second sample, with lower surface area.

Figure 2 shows the DTA profiles of mixtures of Ta and PbO_2 over the composition range from pure Ta up to 20% Ta. The main exotherm in all the compositions is between 586° and 603° . Only the mixtures containing large percentages of PbO_2 show a very small endotherm just before the inception of the main exothermic reaction. This endotherm is easily attributed to the decomposition of Pb_3O_4 to PbO , indicating thereby that the oxidation of Ta metal by PbO_2 takes place concurrently with the dissociation of Pb_3O_4 . Similar observations have been made by Al-Kazraji [6] regarding the oxidation of Si by Pb_3O_4 .

The exotherm due to the oxidation of pure Ta metal or the exotherm at 20% PbO_2 is a single sharp peak. However, the mixtures containing 40–60% PbO_2 also show a second small exotherm, which appears as a broadening at the base

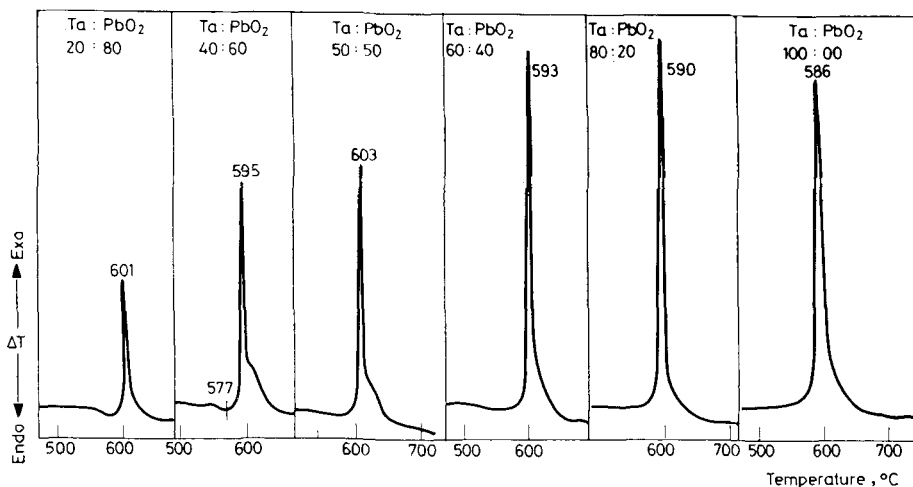
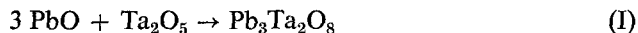


Fig. 2. DTA profiles for Ta– PbO_2 mixtures

in the case of the mixture containing 40% PbO_2 , but becomes a prominent shoulder for 60% PbO_2 . The second exotherm is centred around 605°. This peak is expected to arise from the reaction of PbO and Ta_2O_5 :



The first tantalate contains approximately 60% Pb as PbO , while the second contains approximately 40% Pb as PbO . A number of other tantalates can also be formed due to the reaction between PbO and Ta_2O_5 at round 600°. However, these two tantalates seem to be the most stable and the best characterized [7]. It is proposed that the end-product of the reaction between PbO_2 and Ta at $t > 605^\circ$ is a mixture of a number of tantalates and therefore the second exotherm is due to the formation of tantalates. The IR spectra of the end-products are shown in Fig. 3. Pure Ta_2O_5 has broad bands at 540 and 835 cm^{-1} and weak bands at 325, 730 and 890 cm^{-1} . This agrees with the IR spectra reported by Nyquist [8]. The IR spectra of the end-products of the 60% and 50% PbO_2 mixtures have medium intensity bands at 340 and 540 cm^{-1} and a weak band at 1015 cm^{-1} . The former also shows a shoulder at 610 cm^{-1} and weak absorption at 890 cm^{-1} , while the latter has corresponding frequencies at 650 and 860 cm^{-1} . Stuart [9] has reported a weak absorption at 853 cm^{-1} by the Ta_6O_{11} group of potassium

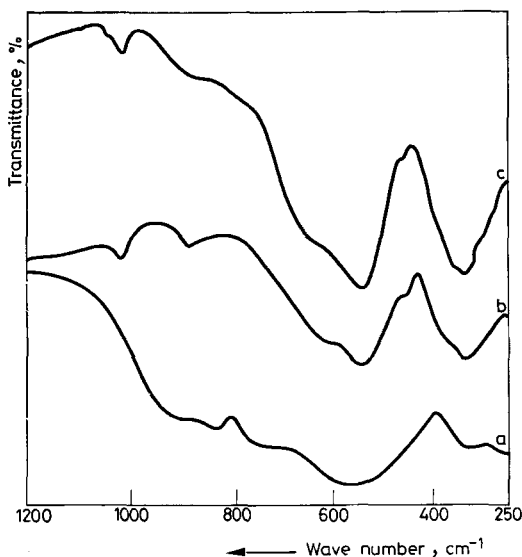


Fig. 3. IR spectra of: a) Ta_2O_5 ; b) residue of Ta— PbO_2 system (40 : 60); c) residue of Ta— PbO_2 system (50 : 50)

tantalate. Sol'nteva [10] has reported a weak but sharp band at 1015 cm^{-1} due to a number of tantalate groupings, and also a variable absorption in the region $660\text{--}840\text{ cm}^{-1}$ due to the tantalate groups in niobium tantalate. It is therefore expected that one may observe a shoulder of variable frequency in the region $650\text{--}830\text{ cm}^{-1}$ in tantalates of varying composition. However, the frequency can be lowered further in the presence of heavy atoms. We therefore postulate that the variable frequency band noticed at 610 or 650 cm^{-1} must be attributed to the presence of tantalates of varying composition.

Rate of oxidation

One significant observation in Fig. 2 is that the peak width of the main exotherm decreases progressively as the oxidizer content increases. Since all the experimental conditions, including the rate of heating, were kept constant, a decrease in peak width should qualitatively describe an increase in the reaction rates. The reciprocals of the half intensity widths of the main exotherm for all the compositions studied here are plotted as a function of the composition in Fig. 4. It may be noted that the reciprocal of the half intensity width will have the dimensions of reciprocal time. A suitable correction for the overlapping second endotherm has been applied in the evaluation of the half width wherever necessary.

Figure 4 shows that the reaction rate between Ta and PbO_2 in air is highly sensitive to the composition in the 40 to 60% concentration range and that the rates are much less sensitive on either side of the 40–60% range.

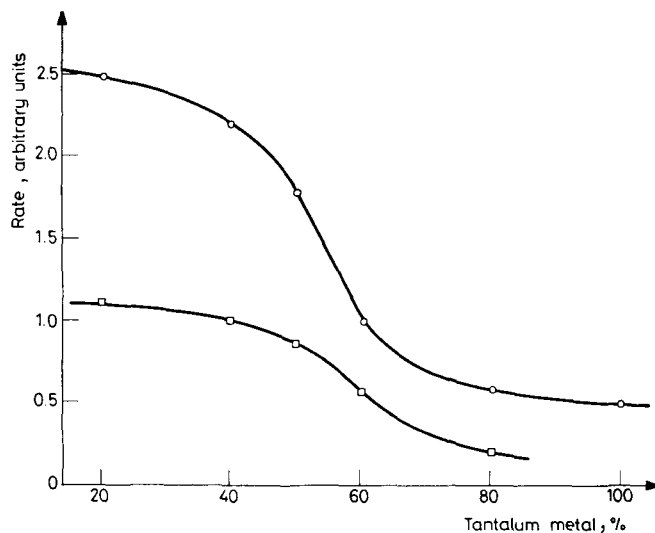


Fig. 4. Rate of oxidation of Ta by PbO_2 and Pb_3O_4 as a function of the oxidizer content

Exothermicity of the oxidation

It is obvious from even a cursory glance at Fig. 2 that the area of the main exotherm decreases progressively as the oxidizer content increases, which means that the heat evolved during the oxidation also decreases in the same order. This is to be expected, because the actual quantity of the metal fuel for constant sample

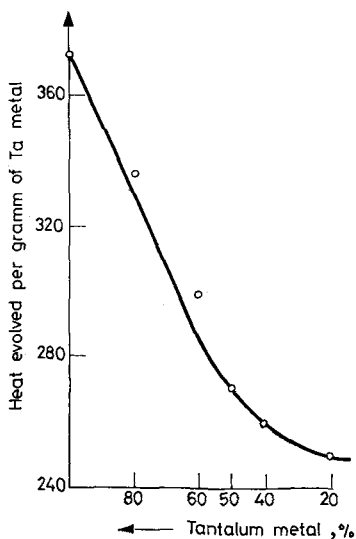


Fig. 5. The apparent exothermicity of oxidation of unit mass of Ta by PbO_2 in mixtures

weight progressively decreases as the oxidizer content increases. If the kinetics and mechanism of the oxidation and other physical factors such as heat conduction and dissipation during the oxidation remain constant the heat evolved and therefore the area under the curve, calculated on the basis of units mass of fuel, should be constant. The calculated area per gram of Ta is plotted as a function of composition in Fig. 5. It is noticed that the measured exothermicity decreases with increasing oxidizer content, which is thermochemically inconsistent. The reason for this lies in the fact that the oxidation proceeds at a very fast rate in the presence of a high oxidizer content, and the factors due to heat loss are more prominent. In fact the oxidation was found to be completed in a few milliseconds in the mixture containing 80% PbO_2 , while the oxidation proceeded smoothly over a few seconds in pure Ta.

Oxidation by Pb_3O_4

Figure 6 shows the DTA profiles of mixtures of Ta + Pb_3O_4 over the composition range from 20% up to 80% Ta metal. The main features of the shape and character of the exotherm are similar to those observed in the case of oxidation

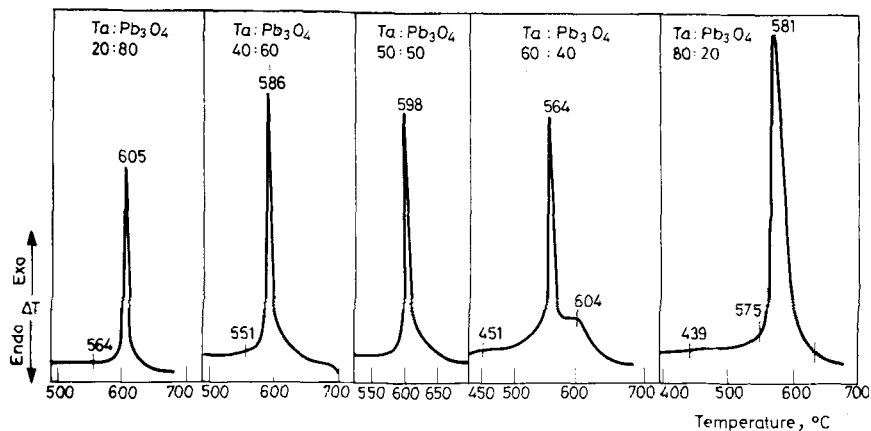


Fig. 6. DTA profiles for Ta–Pb₃O₄ mixtures

by PbO₂. It is to be recalled, however, that the oxidation reaction actually takes place only between Ta and Pb₃O₄, irrespective of whether the mixtures were initially made with PbO₂ or Pb₃O₄. The main interest, therefore, is in the kinetic control of the oxidation by the freshly-formed defective Pb₃O₄ in the case of mixtures made with PbO₂, as against a well-annealed Pb₃O₄. The half intensity widths of the exotherms obtained with Pb₃O₄ mixtures are plotted as a function of composition in Fig. 4, to allow comparison with the PbO₂ system. The rates of oxidation in the case of Pb₃O₄ mixtures are lower than in the PbO₂ system, suggesting that the Pb₃O₄ formed at about 550° in the PbO₂ system is in an active state, and thus PbO₂ is a better oxidizer.

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RÉSUMÉ — La cinétique de l'oxydation des combustibles métalliques par des oxydes métalliques est un des plus importants paramètres dans l'évaluation de l'utilité d'un système métal-oxyde pour des applications pyrotechniques. On a tenté d'étudier l'oxydation du Ta métallique par des oxydants forts comme PbO_2 et Pb_3O_4 , en se servant de l'analyse thermique différentielle et de la spectroscopie infrarouge. La vitesse de l'oxydation du Ta augmente quand la teneur en oxydant augmente pour les systèmes Ta : PbO_2 et Ta : Pb_3O_4 . On propose un mécanisme pour expliquer le phénomène observé.

ZUSAMMENFASSUNG — Die Kinetik der Oxidation metallenthaltener Brennstoffe durch Metalloxide ist einer der wichtigsten Parameter zur Bestimmung der Anwendbarkeit eines beliebigen Metall-Oxid Systems zu pyrotechnischen Zwecken. Es wurde versucht die Oxidation von metallischem Ta durch stark Oxidationsmittel, wie PbO_2 und Pb_3O_4 unter Einsatz der Differentialthermoanalyse und der Infrarotspektroskopie, zu studieren. Die Oxidationsgeschwindigkeit von Ta nimmt mit zunehmendem Gehalt an Oxidationsmittel, sowohl im Ta : PbO_2 — als auch im Ta : Pb_3O_4 — System, zu. Ein versuchsweiser Mechanismus des beobachteten Phänomens wird vorgeschlagen.

Резюме — Кинетика реакций окисления металлических топлив с помощью окислов металлов является одной из важных характеристик при определении выгодности использования какой-либо систем металл-окись. Сделана попытка с помощью дифференциального термического анализа и ИК спектроскопии изучить окисление металла Ta такими сильными окислителями как PbO_2 и Pb_3O_4 . Установлено, что скорость окисления Ta увеличивается с увеличением содержания окислителя в системах Ta : PbO_2 и Ta : Pb_3O_4 . На основе экспериментальных данных предложен механизм наблюдаемого явления.