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OXIDATION OF TANTALUM METAL BY LEAD CHROMATE

R.G. SARAWADEKAR, A.R. MENON and N.S. BANKAR *

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

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ABSTRACT

Differential thermal analysis and gravimetry techniques have been used in the investigation of the tantalum/lead chromate pyrotechnic composition for a range of fuel/oxidant mixtures. Studies include investigation of tantalum and lead chromate individually as well as co-precipitated mixtures, when heated up to approximately 900°C in air and in nitrogen. The kinetics of oxidation of metallic fuels by metal oxides is one of the most important parameters in determining the utility of any metal oxide system in pyrotechnic applications. Infrared spectroscopy has been utilised in an attempt to characterise the reaction products in air and in nitrogen atmosphere.

INTRODUCTION

Binary mixtures of certain fuels and oxidisers are used in pyrotechnic delays. These are described as gasless mixtures and they produce a volume of gas of less than 10 cm^3 g^{-1} during combustion. It is of interest to study such mixtures by employing DTA, TG and DTG techniques. Oxidation of tantalum metal by lead peroxide and red lead have been studied [1]. Mixtures of iron and potassium dichromate were studied by Laye et al. [2]. This technique is also used for ternary mixtures of silicon, boron and potassium dichromate [3]. The use of tantalum metal as a fuel has shown high reactivity with barium chromate without the addition of a more active oxidiser. This is an encouraging feature pointing towards the potential usefulness of other very heavy and pyrotechnically active metals. Tantalum metal always yields Ta_2O_5 in an oxidizing atmosphere and the oxidation reaction is reported as highly exothermic. As no information is available in the literature on this system, we have investigated the system Ta–$PbCrO_4$ employing DTA, TG and DTG in a nitrogen atmosphere and DTA in an air atmosphere, and infrared spectroscopy. The results are described in this paper.

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* To whom correspondence should be addressed.

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MATERIALS

The tantalum metal used had an average particle size of 10.5 μm. The specific surface area was found to be 5710 cm^2 cm^{-3}.

Since these mixtures are highly pyrophoric, they were prepared by the co-precipitation method. The tantalum metal powder samples were suspended in potassium chromate solution with constant stirring, at 70–75°C. Lead nitrate solution (0.1 N) was then added dropwise within 15 min. Stirring was continued for half an hour, after which the precipitate was filtered, washed with distilled water and dried at 100 ± 1°C for 4 h. Mixtures were prepared containing different proportions and were chemically analysed.

MEASUREMENTS

DTA, TG and DTG thermoanalytical curves were recorded on a Netzch thermoanalyzer SA409 in a nitrogen medium using 50 mg samples, a heating rate of 10°C min^{-1} and a maximum temperature of 950°C. DTA profiles were recorded on the DTA instrument described previously [1].

Infrared spectra of slags were recorded in KBr matrix at room temperature on a Perkin–Elmer spectrophotometer model no. 457.

RESULTS AND DISCUSSION

Figure 1 shows the thermoanalytical curves of lead chromate in N_2 medium. The DTA curve shows two endotherms, i.e. a broad peak at ~ 779°C and a sharp peak at 906°C. The first endotherm is attributed to the

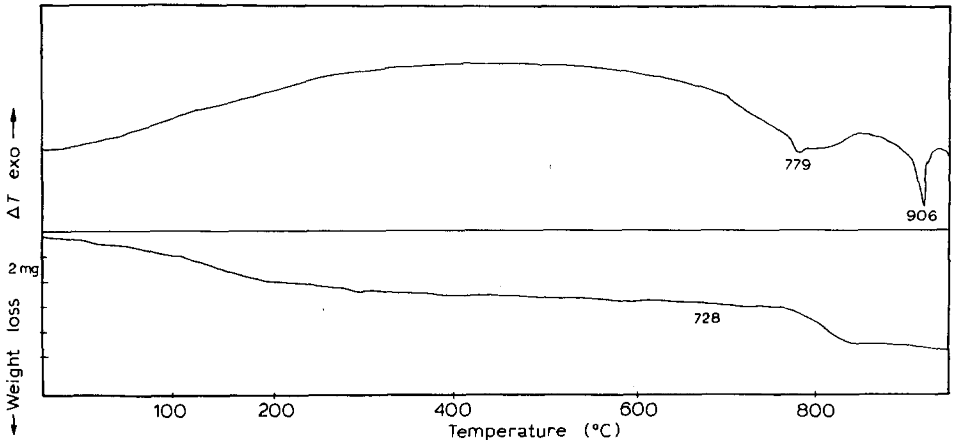

Fig. 1. DTA and TG curves of $PbCrO_4$ in nitrogen.

phase transition in the temperature range 760–820°C which is due to the $\beta \rightarrow \alpha$ transformation and the second endotherm is due to melting of PbO [4]. Lead chromate heated in air shows a slight but steady gain in weight in the range 812–904°C [5].

The TG data show a loss in weight in two steps. The first step is in the range 55–728°C and shows a weight loss of about 10% which is due to removal of adsorbed water associated on the lead chromate. The second step shows a 6% weight loss which is due to evolution of oxygen gas in the range 728–830°C: this is rather higher than the calculated value of 4.95%. From this, the equilibrium of decomposition may be represented by

$$2\ PbCrO_4 \rightarrow 2\ PbO + Cr_2O_3 + 1.5\ O_2 \qquad (1)$$

Hampel and Schubert [6] found that evolution of gas began at 600°C and they observed that rather more oxygen was given off up to 1150°C, than that calculated from the equation

$$4\ PbCrO_4 = 2\ Pb_2OCrO_4 + Cr_2O_3 + 1.5\ O_2 \qquad (2)$$

Equation (2) gives a weight loss of up to 3.65% for evolution of oxygen. It is clear that eqn. (1) gives a good representation of the decomposition of $PbCrO_4$.

The final reaction product was a solid mixture of PbO and Cr_2O_3, the presence of which was confirmed by the infrared spectra of the slags as shown in Fig. 2. Pure $PbCrO_4$ shows bands at 850, 885, 370 and 382 cm^{-1} which are attributed to symmetrical, asymmetrical and bending frequencies of the CrO_4 group [7]. The slag obtained shows the presence of Cr_2O_3 which

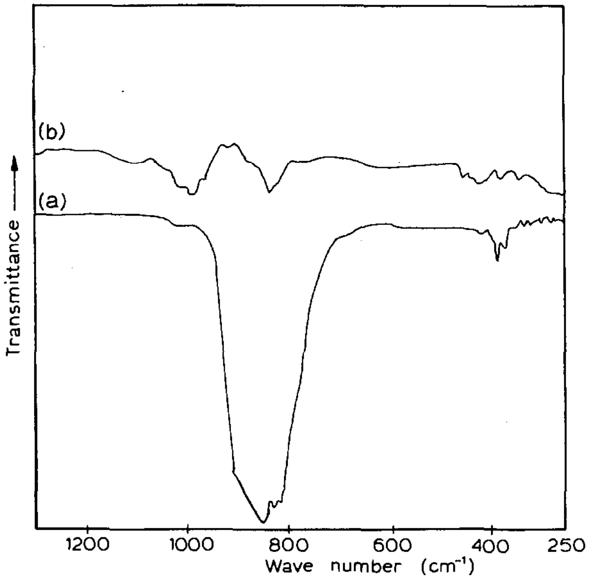

Fig. 2. IR spectra of (a) $PbCrO_4$ and (b) $PbCrO_4$ heated to 900°C.

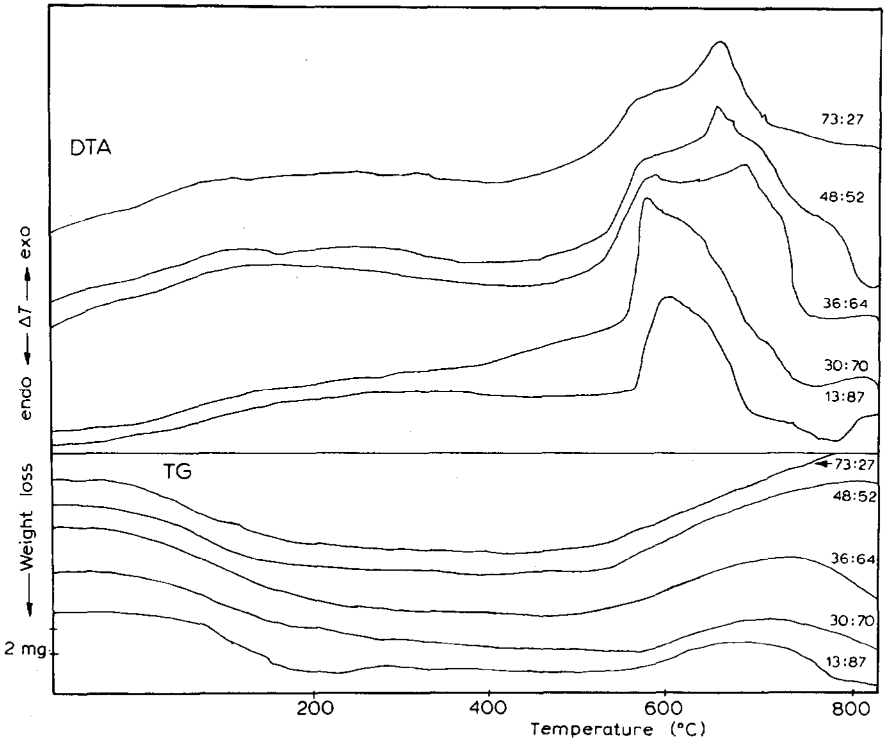

Fig. 3. DTA and TG curves of Ta + $PbCrO_4$ mixtures in nitrogen.

gives bands at 970 and 830 cm^{-1} due to the double bond character and Cr–O–Cr bonding: PbO gives a band at 440 cm^{-1} due to Pb–O [8].

Figure 3 shows the DTA and DTG curves of Ta–$PbCrO_4$ mixtures in a nitrogen atmosphere. The DTA curve shows a broad exotherm for the mixtures containing 13 and 30% tantalum and two broad peaks for other compositions. The first peak appears in the temperature range 568–583°C and the second peak appears between 646 and 671°C. The first peak is prominent in the mixtures containing 13 and 30% tantalum metal. Both peaks are prominent and indicate an equal rate of reaction. The second peak is prominent in the compositions containing 49 and 73% tantalum metal. Thus, the DTA profiles indicate that the oxidation of tantalum takes place before the decomposition of lead chromate and it shows that $PbCrO_4$ combines directly with tantalum metal. A reaction mechanism can be given, viz.

$$10\ PbCrO_4 + 6\ Ta \rightarrow 3\ Ta_2O_5 + 10\ PbO + 5\ Cr_2O_3$$

But the second exotherm is due to the formation of tantalum nitride.

$$2\ Ta + N_2 \rightarrow 2\ TaN$$

The TG data (Table 1) shows that after 583°C the mixture increases in

TABLE 1

Thermoanalytical data

Mixture Ta : $PbCrO_4$	TG steps		Gain in weight (%)
	Range (°C)	Peak temp. (°C)	
13 : 87	553–666	583	4.8
30 : 70	533–583	566	
	583–618	618	5.2
36 : 64	488–617	578	
	617–680	671	10.2
48.52	526–618	568	
	618–770	646	14.0
73 : 27	518–603	568	
	603–700	646	14.4

weight. As the oxidiser content decreases, the nitride formation increases: this is well supported by the TG data. From 4.8%, the weight loss increases up to 14.4% in a mixture. The formation of nitride is reported by Von Bolten [9].

The oxidation of Ta metal in N_2 medium is very slow. Figure 4 shows IR spectra of slags obtained from Ta + $PbCrO_4$ systems in N_2 atmosphere. The bands were recorded in the ranges 300–350 cm^{-1} and 530–640 cm^{-1}. As the

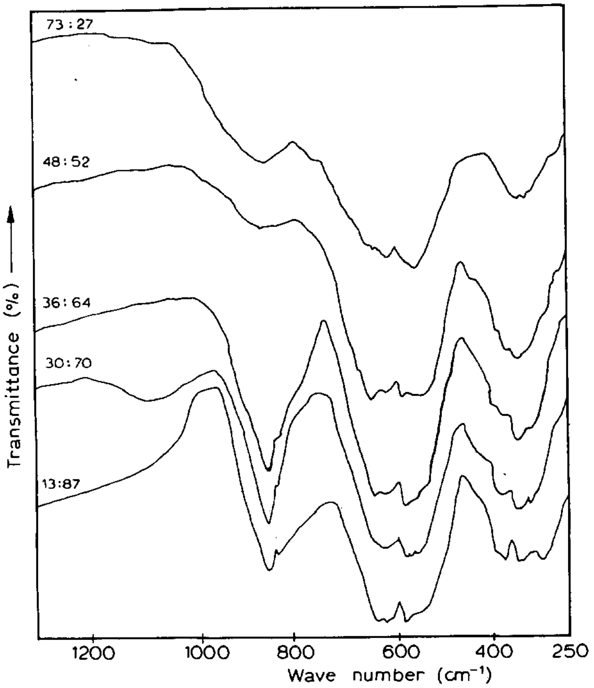

Fig. 4. IR spectra of the final products of Ta + $PbCrO_4$ systems in nitrogen.

oxidiser content increases, the intensity of the peaks increases. From this we can conclude that various types of tantalates are formed. The formation of various tantalates has been reported [10].

Oxidation of tantalum in air

Figure 5 shows the DTA profiles of Ta–$PbCrO_4$ mixtures in air over the composition range from pure tantalum up to 13% Ta. The main exotherm in all the compositions is between 523 and 711°C. As the oxidiser content of the mixture increases, the rate of oxidation reaction decreases. At the 73 : 27 composition, the reaction takes place at 643°C while at higher percentages of $PbCrO_4$ the reaction temperature increases up to 657°C. In all the cases, a single peak is observed and the exotherm for the 27% $PbCrO_4$ mixture is a single sharp peak. It forms a lead chromium tantalate (Pb_2CrTaO_6). A number of other tantalates can also be formed due to the reaction between PbO and Ta_2O_5 at around 600°C. Thus, the end-product of the reaction between $PbCrO_4$ and Ta at $T > 620°C$ is a mixture of a number of tantalates. The IR spectra of the end-products are shown in Fig. 6. Pure Ta_2O_5 has broad bands at 540 and 835 cm^{-1} and weak bands at 325, 730 and 840 cm^{-1}. This agrees with the IR spectra reported by Nyquist and Kagel [11]. The IR spectra of the end-products of various mixtures have broad bands 300–350 and 530–640 cm^{-1}. As the oxidiser content in the mixture increases, the intensity of these peaks increases. These bands have been reported for tantalate groups [11]. From these results, we postulate that the frequency bands at 580 and 610 cm^{-1} must be attributed to the presence of tantalates of varying compositions.

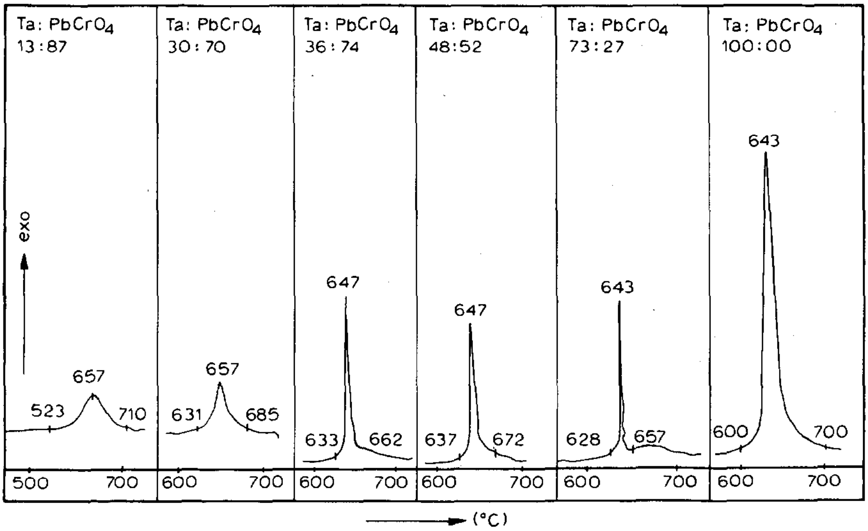

Fig. 5. DTA profiles for Ta + $PbCrO_4$ mixtures in air.

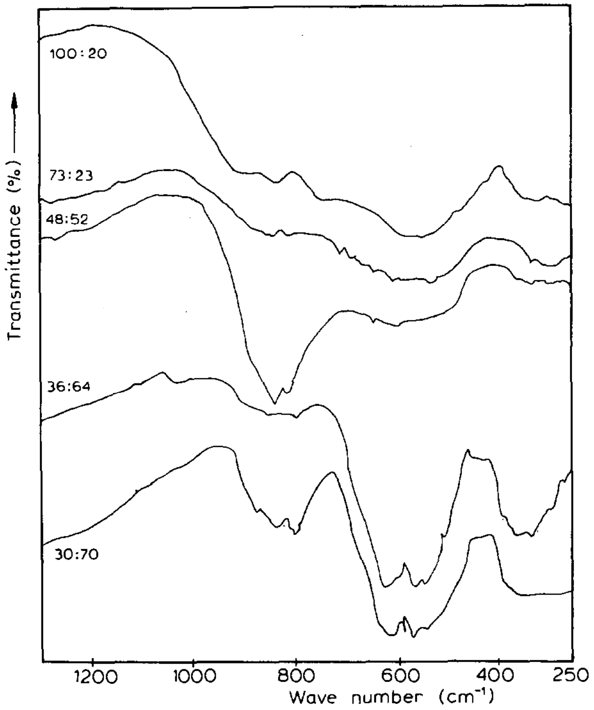

Fig. 6. IR spectra of the final products of Ta + $PbCrO_4$ systems in air.

Rate of oxidation in air

In Fig. 5 the peak width of the main exotherm decreases progressively as the oxidiser content increases. Under identical experimental conditions, a decrease of peak width should therefore qualitatively describe the variation 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. 7(a). As the tantalum percentage increases, the rate of the reaction increases and reaches a maximum around 70–80% Ta, and then gradually decreases.

Exothermicity of the oxidation in air

The area of the main exotherms decreases as the oxidiser content increases: this can be observed in Fig. 5. This means that the heat evolved during the oxidation also decreases in the same order. 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 so the area under the curve calculated on the basis of a unit mass of fuel should be constant. The area so calculated is plotted as a function of

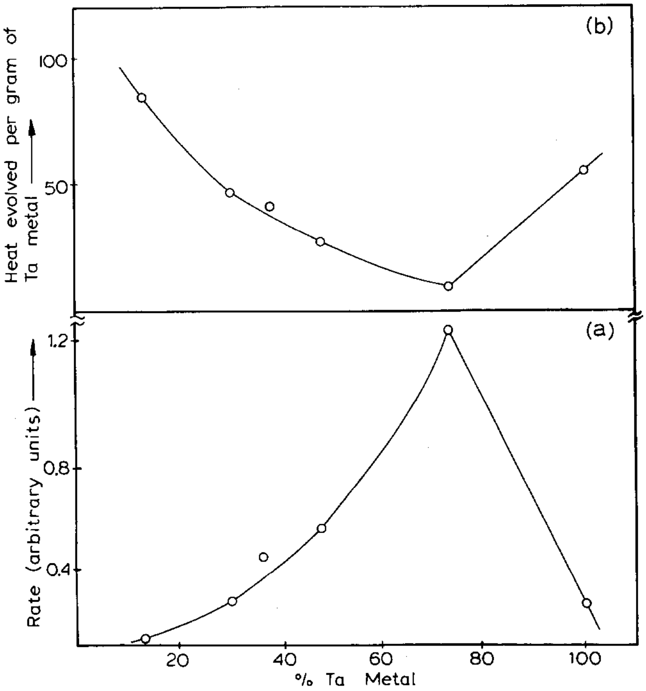

Fig. 7. (a) Rate of oxidation of Ta by $PbCrO_4$. (b) The apparent exothermicity of the oxidation of unit mass of Ta by $PbCrO_4$ in mixtures.

composition in Fig. 7(b). It is noticed from Fig. 7(b) that the measured exothermicity decreases as the oxidiser content decreases. The oxidation was found to be completed in a few milliseconds for the mixture containing 27% $PbCrO_4$, while the oxidation of pure tantalum proceeded smoothly for a few seconds.

It is concluded that tantalum metal reacts with lead chromate before its decomposition in both air and nitrogen atmosphere. The rate of reaction is faster in air than in nitrogen.

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