

Thermodesorption Studies on Al Nanopowders

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Abstract: Aluminium (Al) nanopowder has been shown to possess unique thermal behaviour and to enhance the performance of some energetic materials (EM). However, Al nanopowder has a high reactivity with water, which causes "aging" of Al nanopowder, and consequent reduction in its effectiveness in EM compositions. Water adsorption and desorption is a particular concern, since the aging reaction of Al nanopowders may be related to the water adsorbed on its surface. The thermodesorption of adsorbed gases on nanometer-sized aluminium powders was investigated using Thermogravimetry (TG) and Thermogravimetry-Fourier Transform Infrared-Mass Spectrometry (TG-FTIR-MS). The results show that the Al nanopowder studied contains 12 mass % of adsorbed gases. Desorption of water and carbon dioxide was observed by FTIR and MS. The kinetic parameters for the desorption of the adsorbed gases were determined using variable heating rate and isothermal studies. The activation energies of desorption obtained from the various methods are compared.

Key words: physical chemistry; aluminium; nanometer-sized; thermal; desorption; kinetic

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1 Introduction

Aluminium (Al) powder is commonly added to explosives, propellants and pyrotechnic compositions to improve their performance. Conventional weapons-grade Al powder is typically micron-sized. Recent advances in metal processing technology have allowed sub-micron particles to become commercially available^[1,2]. Incorporation of Al nanopowder results in an increase in the burn rate and enhancements in detonation properties^[3,4].

One explanation for the unique rate-enhancement behaviour of Al nanopowder is the higher reactivity associated with the larger surface area of Al nanopowder compared to micron-sized Al powder. Al nanopowder exhibits a strong exotherm peak in air at temperatures that are 100–200 °C below the melting point of Al, due to the oxidation of the particles, a phenomenon only observed with nanoscale powders^[5]. On the other hand, Al nanopowder also has a high reactivity with water and produces aluminium oxide (Al₂O₃) or bayerite (Al(OH)₃)^[5,6]. The reactivity of Al nanopowder with water has been shown to cause aging of Al nanopowder^[5,6]. Subsequent use of the aged material in explo-

sives and propellant compositions would result in significant losses in performance. Earlier outgassing studies have shown the presence of adsorbed water and carbon dioxide on the surface of various Al nanopowders^[7]. The adsorption of H₂O and CO₂ on Al nanopowders is also particle size dependent, with more being adsorbed as the particle size decreases^[7]. Water adsorption and desorption is a particular concern in the aging study of Al nanopowders, since the aging reaction of Al nanopowders may be related to the water adsorbed on its surface. Therefore, it is of interest to study water desorption from Al nanopowder.

Temperature programmed desorption (TPD) is one of the most frequently employed techniques in surface science and catalysis. After appropriate calibration, it can be used to determine surface coverages of adsorbates and to evaluate the activation energy of desorption. TPD measurements have been used to identify the desorbed gases from metal powders^[9]. TPD only requires a small amount of sample for its measurement and is thus suitable for quick screening of materials. Analysis of the spectrum provides information on the activation energy of desorption for each desorbing species.

The aim of this work is to study the thermodesorption of adsorbed gases on Al nanopowder using Thermogravimetry (TG) and TG interfaced to Fourier Transform Infrared and Mass Spectrometers (TG-FTIR-MS). In this paper,

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the desorption kinetics of the adsorbed gases for an Al nanopowder are presented.

2 Experimental

2.1 Materials

The Al nanopowder, Alss was obtained from Aveka Inc. and was produced by a high rate evaporative method^[2]. The particle size of Alss was in the range of 20–30 nm, and the initial oxide content was about 10 mass %. Alss was stored in a desiccator under argon at room temperature, and was used as received.

2.2 Thermogravimetry

A TA Instruments 5200 Thermal Analysis System with a TG 2950 module was used for the TPD measurements on Al nanopowder. Both variable heating rate and isothermal methods were performed to study the thermal desorption of gases from the surface of Al nanopowders.

For the variable heating rate study, about 2 mg of Alss were heated at $1-20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature to $350\text{ }^{\circ}\text{C}$. The TG isothermal experiments were performed at isothermal temperatures of $50-100\text{ }^{\circ}\text{C}$. The samples ($\sim 2\text{ mg}$) were heated at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to the selected isothermal temperature and then held isothermally for 100 min. All TG experiments were performed with Al open pans and a dry nitrogen purge of $60\text{ cm}^3\cdot\text{min}^{-1}$ in the furnace and $40\text{ cm}^3\cdot\text{min}^{-1}$ in the balance chamber.

The TG was calibrated for mass and temperature^[10]. To confirm the baseline of the TG, experiments were performed on an empty Al pan using the minimum and maximum heating rates. The TG drift from both runs was about $+17\text{ }\mu\text{g}$ over the entire temperature range, which represents 0.8 mass % for 2 mg of sample.

2.3 TG-FTIR-MS

The TA 5200 Thermal Analysis System with a simultaneous Thermogravimetry-Differential Thermal Analysis (TG-DTA) 2960 module was interfaced to a Bomem MB100 Fourier Transform Infrared Spectrometer (FTIR) and a Balzers Thermostar GSD300 Quadruple Mass Spectrometer (MS) for the thermodesorption studies. The TG-FTIR-MS data were acquired simultaneously to identify the gases that desorbed while the samples were heated.

Approximately 4 mg of Alss were placed in alumina pans. The reference consisted of an equal amount of plati-

num foil. The system was purged with $50\text{ cm}^3\cdot\text{min}^{-1}$ of helium. The samples were heated from 30 to $350\text{ }^{\circ}\text{C}$ at six different heating rates between 10 and $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in the variable heating rate study. For the isothermal study, the samples were heated at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to the selected isothermal temperature, and then held isothermally for 60 min in helium. The isothermal temperatures were 80, 90, 100, 110 and $120\text{ }^{\circ}\text{C}$. TG mass and temperature^[11] calibrations were performed prior to the experiments. The TG-FTIR-MS system was pre-flushed with $180\text{ cm}^3\cdot\text{min}^{-1}$ of helium for 30 min prior to each experiment.

The FTIR interface consisted of a 5 mm i. d. Teflon tube and a 10 cm Pyrex cell with a 50 cm^3 volume and KBr windows. A quartz microfibre filter was placed at the FTIR inlet. The acquisition rate of the FTIR was two scans every minute and the time delay was about 10 s from the TG-DTA furnace outlet to the FTIR cell.

For the MS analysis, the heated quartz capillary interface was placed near the sample pan, in the TG-DTA furnace. Data were acquired using bargraph scan from 5 to 100 amu (atomic mass unit) at a speed of $0.2\text{ s}\cdot\text{amu}^{-1}$. The electron multiplier detector was set at 960 V for acquisition. The MS was calibrated for mass alignment and amplifier signal.

To confirm the baseline of the TG-FTIR-MS, an experiment using the same heating profile was performed on two empty alumina pans. The TG drift was about $+7.3\text{ }\mu\text{g}$ over the entire temperature range, which represents 0.2 mass % for 4 mg of sample. The FTIR and MS baseline results were used to assess the empty pan background noise.

3 Results and discussions

3.1 TG variable heating rate study

The typical mass loss behaviour for Alss is shown in Fig. 1, where the mass loss and the derivative of mass loss with respect to time are plotted versus temperature. A mass loss of $(11.9 \pm 0.7)\%$ was obtained from Alss, which implies that about 12 mass % of gases are adsorbed on Alss at room temperature.

These adsorbed gases desorb in two steps from Alss. The initial step of about 1 % was observed below $40\text{ }^{\circ}\text{C}$. This initial mass loss represents the desorption of adsorbed gases on the surface of Alss remote from the monolayer.

The monolayer is a layer of adsorbed gases which is in direct contact with the Alss surface. The second step reflects a gradual thermodesorption of the monolayer of adsorbed gases with a maximum rate at about 130 °C (Fig. 1).

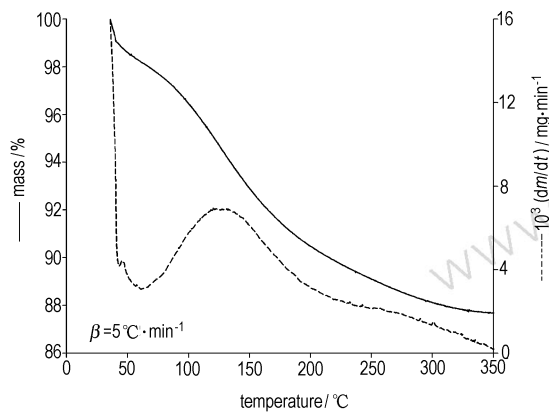


Fig. 1 TG and DTG curves for Alss

The results obtained from the TG measurements conducted at several heating rates show that the maximum of the derivative TG (DTG) curve varied with the heating rate. The temperature at the maximum of the DTG curve is labeled T_p , and the dependence of T_p on the heating rate was used to determine the kinetic parameters for the desorption of the adsorbed gases. The rate of desorption can be described using the Polanyi-Wigner equation^[12],

$$-\frac{d\theta}{dt} = k\theta^n \quad (1)$$

where θ is the surface coverage of adsorbate (a dimensionless ratio of actual adsorbate to that required to cover the entire surface), t is the time, n is the order of desorption, k is the rate constant in the Arrhenius equation

$$k = v \exp\left[\frac{-E}{RT}\right] \quad (2)$$

where v is the pre-exponential factor of desorption, E is the activation energy of desorption, R is the gas constant, and T is the temperature. T and t are related by the heating rate $\beta = dT/dt$.

In the variable heating rate method described by Falconer et al^[13], a logarithmic plot of β/T_p^2 versus $1/T_p$ gives a straight line with slope equal to $-E/R$. The method requires the same initial coverage and assumes that the coverage left on the surface at T_p is the same for all the heating rates.

In Fig. 2, an activation energy of $(178 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$

was obtained for the desorption of the adsorbed gases on Alss. The activation energy agrees with the values reported previously for the desorption of water from alumina ($120 - 200 \text{ J} \cdot \text{mol}^{-1}$)^[8]. Since Al nanopowder contains a passivating layer of Al_2O_3 , the activation energy of desorption for Alss may be similar to that obtained for alumina.

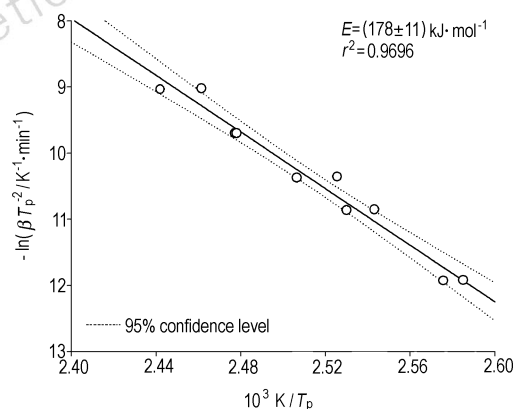


Fig. 2 TG variable heating rate study

3.2 TG isothermal study

The desorption kinetics of the adsorbed gases for Alss were also investigated using an isothermal study. Isothermal TG experiments were conducted at several temperatures between 50 °C and 100 °C.

The TG results are plotted as $\ln(k)$ against $1/T$ for three values of n : 0, 1 and 2, which are the orders frequently observed in desorption studies^[8]. Fig. 3 shows that the plot for $n = 2$ has the highest correlation factor. Hence, the desorption order for the adsorbed gases on Alss is close to 2. Values of $E = (30 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$ and $\ln(v/\text{min}^{-1}) = 3.9 \pm 0.8$ were determined from the slope and the intercept, respectively, using $n = 2$.

There is a large variation in the activation energies obtained from the variable heating rate and the isothermal studies. This difference may result from the different temperature ranges used in the studies. The temperature range for the variable heating rate study (Fig. 1) is higher than that for the isothermal study (Fig. 2).

The activation energy of desorption may also vary with the different adsorbate coverage in the two studies. In the variable heating rate study, the activation energy was determined using the peak temperatures, which were observed at an adsorbate coverage of about 0.6. For the isothermal study, the rate constants in Fig. 3 were calcu-

lated at an adsorbate coverage of about 0.8. The kinetic parameters for desorption have been shown to depend on the adsorbate coverage due to the interactions between adsorbate particles^[8]. If the activation energy for the desorption of the adsorbed gases on Alss is strongly dependent on the adsorbate coverage, the slight differences in adsorbate coverage in the two TG studies may cause a significant variation in the results.

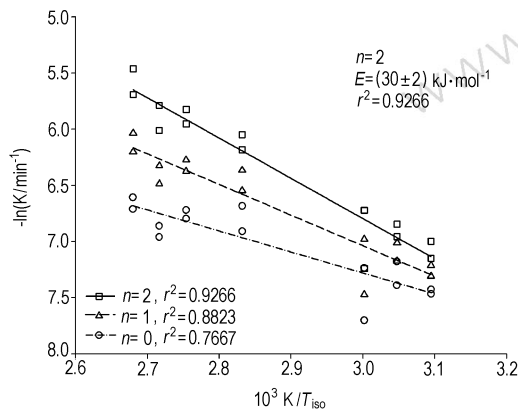


Fig. 3 TG isothermal study

The variation in the kinetic parameters may also be due to the concurrent desorption of different adsorbed gases. In the variable heating rate study, the peak temperature may only depend on the desorption of the dominant adsorbed gas, whereas the desorption rate from the isothermal study may include that from both desorbed gases. In order to separate the desorption of different adsorbed gases, and to investigate the desorption kinetics of these adsorbed gases from Alss, the study was supplemented by TG-FTIR-MS experiments.

3.3 TG-FTIR-MS variable heating rate study

Example plots for the TG-FTIR-MS results for Alss at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ are shown in Fig. 4. The TG mass loss and the derivative of mass loss with respect to time are plotted versus temperature in Fig. 4(a). The absorbance A versus temperature for the evolved gases, which were detected by FTIR, are shown in Fig. 4(b). The MS data are presented as ion current versus temperature for the selected mass fragments in Fig. 4(c).

A mass loss of about 11% was obtained for Alss (Fig. 4(a)) and it is consistent with the second mass loss obtained from the TG study (Fig. 1). The initial step obtained from the TG study (Fig. 1) was not observed

from the TG-FTIR-MS results. As discussed earlier, this initial mass loss of 1% represents the desorption of adsorbed gases on the surface of Alss remote from the monolayer. These adsorbed gases may have already desorbed prior to the experiment when the TG-FTIR-MS system was being pre-flushed.

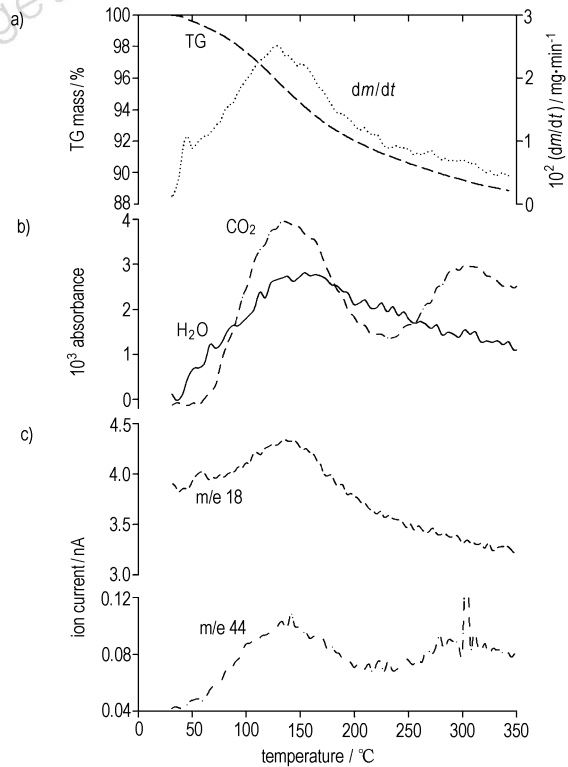


Fig. 4 TG(a), FTIR(b), MS(c) results for Alss heated at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in helium

The FTIR and MS results show that the desorbed species were water and carbon dioxide (Fig. 4(b) and (c)). The single peak evolution of H_2O with a maximum of $\sim 150\text{ }^{\circ}\text{C}$ suggests a desorption of intact H_2O molecules from the Alss surface. Within the temperature range of the experiments, the FTIR and MS results show no dissociatively adsorbed water on the surface of Alss. Two separate peaks were observed for CO_2 at about 134 and $300\text{ }^{\circ}\text{C}$. This observation suggests that CO_2 desorbs via two steps from Alss. These two steps result from two different mechanisms of thermodesorption. This difference may be caused by multilayers of CO_2 on Alss, and/or CO_2 adsorbed on non-uniform surfaces of the sample.

As shown in Fig. 5, the activation energy for the desorption of H_2O and CO_2 (lowest temperature peak) de-

terminated using the variable heating rate method varies between $40 \text{ kJ} \cdot \text{mol}^{-1}$ and $54 \text{ kJ} \cdot \text{mol}^{-1}$. The results obtained by FTIR and MS are similar. No significant difference was observed between the desorption energies for H_2O and CO_2 . The error for the CO_2 desorption detected by MS is larger than the others. This error may result from the low intensity of MS CO_2 curve, since more uncertainties may be involved during the selection of the peak temperatures.

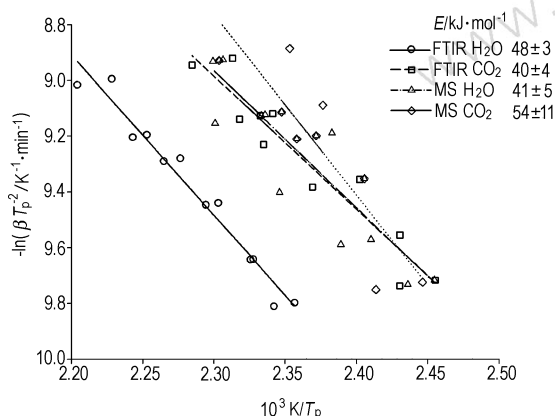


Fig. 5 FTIR and MS variable heating rate results

3.4 TG-FTIR-MS isothermal study

The thermodesorption of H_2O and CO_2 from Alss was further investigated using a TG-FTIR-MS isothermal study. The FTIR results obtained at five different isothermal temperatures show that the peak height is temperature dependent. This is illustrated for both H_2O and CO_2 for three of the temperatures in Fig. 6.

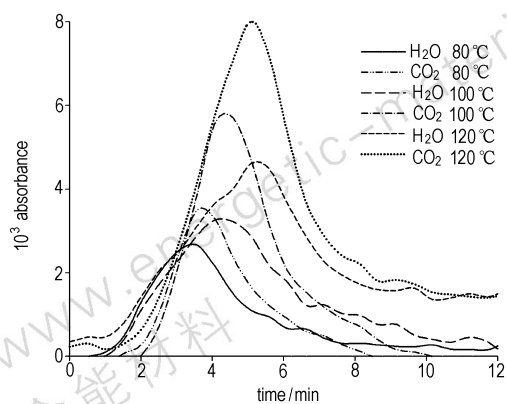


Fig. 6 FTIR results at various isothermal temperatures

As shown in Fig. 7, the logarithm of the maximum absorbance (A_{max}) for H_2O and CO_2 is linearly related to the

inverse of the temperature. Activation energies of (16 ± 2) and $(23 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$ were obtained for the desorption of H_2O and CO_2 , respectively.

For the MS results, the maximum intensity seems to vary with the isothermal temperatures. However, the activation energy cannot be determined due to the low intensity, which was significantly affected by the baseline noise.

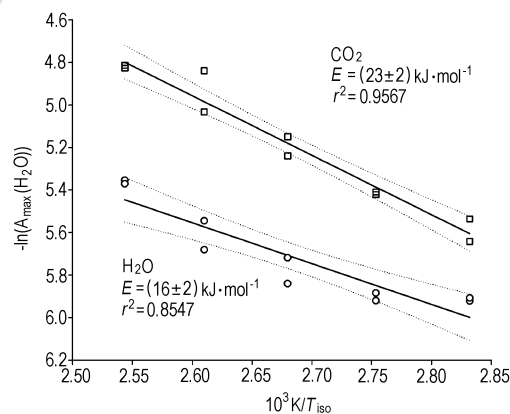


Fig. 7 FTIR isothermal results

The activation energies of desorption for the adsorbed gases on Alss obtained from the TG isothermal results, the FTIR and MS variable heating rate results and the FTIR isothermal results are of the same magnitude. However, the activation energy obtained from the TG variable heating rate study deviates from that obtained by the other methods. The large variation in the activation energies obtained from the various methods may result from the different temperature ranges used in the studies. The activation energy may also vary with the different adsorbate coverage in the two studies, since the kinetic parameters for desorption depend on the adsorbate coverage.

Another possible explanation for the differences in kinetic parameters is that the assumptions made in the variable heating rate method are not valid. This method assumes that only one layer of adsorbed gases is present on the surface and the initial adsorbate coverage is constant^[13]. Alss could have multilayers of water and/or carbon dioxide. As discussed earlier, the thermodesorption of multilayers of CO_2 was demonstrated by the FTIR and MS results.

Additionally, the samples used in the TG and TG-FTIR-MS measurements may not have a constant initial adsorbate coverage.

4 Conclusions

Thermodesorption studies using TG and TG-FTIR-MS were performed on an Al nanopowder. The Al nanopowder studied contained 12 mass % of adsorbed gases. The FTIR and MS results show that the adsorbed gases were water and carbon dioxide. Kinetic parameters for the desorption of the adsorbed gases were determined using both variable heating rate and isothermal studies.

Activation energies of $(178 \pm 11) \text{ kJ} \cdot \text{mol}^{-1}$ and $(30 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$ were obtained from the TG variable heating rate and isothermal studies, respectively. For the TG-FTIR-MS studies, the activation energy of desorption for H_2O and CO_2 obtained from the variable heating rate and isothermal methods varied between $16 \text{ kJ} \cdot \text{mol}^{-1}$ and $54 \text{ kJ} \cdot \text{mol}^{-1}$.

There is a large variation in the activation energies obtained from the various methods. The differences may result from the different temperature ranges and the different adsorbate coverage, which vary with the different methods used for the estimation of the activation energy. Variation in the kinetic parameters may also be due to the invalid assumptions made in the methods, as follows (i) a monolayer of adsorbed gases and (ii) a constant initial adsorbate coverage.

Similar desorption energies were obtained for H_2O and CO_2 (lowest temperature peak), which implies that H_2O and CO_2 interact in a similar manner with the surface of Alss.

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纳米 Al 粉的热脱附研究

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摘要: 纳米 Al 粉有独特热行为,能增强某些含能材料的性能。然而,纳米 Al 粉与水的反应性高,导致纳米 Al 粉“老化”,降低了它在含能复合材料中的作用。由于纳米 Al 粉的老化反应与吸附至其表面的水有关,因此应特别关注水的吸、脱附作用。本文用 TG 和 TG-FTIR-MS 研究了纳米 Al 粉吸附气体的热脱附。结果表明,所研究的纳米 Al 粉含 12% (质量) 的吸附气体。用 FTIR 和 MS 检测到水和 CO_2 的脱附。用多重加热速率和等温研究,得到了吸附气体的脱附过程动力学参数。对不同方法得到的脱附活化能进行了比较。

关键词: 物理化学; Al; 纳米尺寸; 热作用; 脱附; 动力学

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