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THERMAL CHARACTERIZATION OF PASSIVATED NANOMETER SIZE ALUMINIUM POWDERS

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Abstract

The thermal properties of Alex, a nanosized Al powder, were determined using various techniques, including DSC, TG, simultaneous TG-DTA (SDT) and accelerating rate calorimetry (ARC). The results demonstrate that the specific heat capacities of nano and micron size Al powders are similar between 30 and 400°C. Dynamic and isothermal methods were used to determine the kinetic parameters for the oxidation reaction of Alex, which was detected at an onset temperature of 481°C. The results obtained were in good agreement with each other. From the ARC experiments, exotherms were detected near 340 and 260°C for experiments started at ambient pressure and at 0.72 MPa, respectively.

Keywords: aluminium, ARC, DSC, kinetics, nanometric size, SDT, TG

Introduction

Alex, a nanosized Al powder produced by the electro-explosion process, has been shown to possess unique thermal behaviour, which renders it useful as a fuel in both propellant and explosive formulations. Propellants containing nanosized Al powder have considerably enhanced burning rates over those containing micron size powder [1]. In some cases the burning rates of propellants with Alex were as much as 5 to 20 times greater. The exact mechanism responsible for the unique rate-enhancement behaviour of Alex powder in propellants is not known. One explanation is the higher reactivity associated with the larger surface area of Alex compared to micron sized Al powder. Ismail *et al.* [2] determined that the particle diameter of Alex powder was 183 nm, compared to 6 to 100 μm for some typical Al powders presently used in propellant formulations. They also determined that the Alex powder had an aluminium oxide coating thickness of 1.9 nm.

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Previous thermal analysis studies conducted by Mench *et al.* [3] have indicated that when Alex powder is heated in air or nitrogen environment, an exotherm occurs at onset temperatures of 548 and 680°C, respectively. These studies showed that these significant exotherms are unique to Al nano powder. Compared to the micron sized Al powder, the reactions of Alex occur at a lower temperature with a higher rate of reaction. Aumann *et al.* [4] have demonstrated that the activation energy for the oxidation of nano Al powder with average particle size from 24 to 65 nm was 49 kJ mol^{-1}, which is smaller than the value of 165 kJ mol^{-1} for 0.25 mm thick Al strip.

This paper reports a detailed study of the thermal properties of Alex, including the heat capacity, kinetic parameters for oxidation obtained by various techniques and exothermic activity in an oxidative environment by adiabatic calorimetry.

Experimental

Nano and micron size Al powders were received from Defence Research Establishment Valcartier and used without further treatment. The powders were stored in a dessicator under argon.

DSC

For the specific heat capacity measurements of nano and micron size Al, in accordance with the ASTM E1269 method [5], a 2100 Thermal Analysis System with a 2910 DSC module equipped with a pressure cell was used. The cell was evacuated and then flushed with helium to remove any traces of air. All experiments were carried out in a helium purge of 50 mL min^{-1}. The cell was heated from 30 to 400°C at 5°C min^{-1}. Aluminium hermetic pans with a laser drilled pin-hole (75 μm) vented lid were used. Synthetic sapphire powder (30 mg) was used as the reference material in order to calibrate for heat capacity. The sample size for Alex and the micron Al powder was about 5.0 mg. The DSC was calibrated for heat flow and temperature using a helium purge and SRM standards indium and lead. The cell constant was set to a value of 1 before conducting the experiments, as recommended by the manufacturer (TA Instruments). All the pans and lids were cleaned by heating to 450°C in an oven before use.

For the thermal studies of Alex up to 600°C in helium and nitrogen, the pressure cell was used to ensure a pure helium or nitrogen purge. The procedure used to remove any traces of air is described above. The Al hermetic pan with pin-hole lid containing 3.0 or 5.0 mg of Alex was heated from 400 to 600°C at 0.5°C min^{-1}. The slow heating rate was used to ensure the reaction would be complete below the melting point of the Al sample container. The purge gas flow rate was 50 mL min^{-1}. In order to compare the effects, experiments were also performed with Alex in air and with empty pans in helium under the same conditions. For the thermal studies of Alex up to 600°C, the DSC was calibrated for heat flow and temperature using nitrogen and a heating rate of 0.5°C min^{-1} with SRM standards indium, lead and zinc.

TG

A TA 2100 Thermal Analysis System with a TG 2950 module was used. Prior to the isothermal studies for the determination of kinetic parameters, dynamic experiments at 10°C min^{-1} were carried out to select the appropriate isothermal temperatures. Isothermal experiments were conducted between 480 and 520°C. The sample was heated at a rate of 100°C min^{-1} to the desired temperature and then kept isothermal until it reached the maximum mass gain. An alumina pan containing about 5.0 mg of sample was used. Dry air was used as the purge gas at a flow rate of 60 mL min^{-1} for the furnace and 40 mL min^{-1} for the balance chamber.

The TG was calibrated for mass and temperature. The standard reference mass used for mass calibration was checked *vs*. a Mettler M3 microbalance with a precision of ±1 μg. The temperature was calibrated using the Curie Point magnetic method with SRM nickel [6].

SDT

A TA 2100 Thermal Analysis System with a SDT 2960 module was used for the kinetic study. The TG-DTA data were acquired simultaneously in one run. Heating rates from 1 to 5°C min^{-1} were used, following the procedures of ASTM E698 [7] and E 1641 [8]. The reference material was platinum foil. Approximately 5 mg of sample and reference were placed in alumina pans and heated from 30 to 700°C, with 100 mL min^{-1} of dry air purge.

TG mass, DTA baseline and temperature calibrations were performed prior to the experiments. To confirm the baseline of the SDT, two empty alumina pans were heated at 5°C min^{-1} to 700°C. Temperature calibration was carried out at each heating rate using an indium SRM standard and high purity Al wire. The thermal resistance of the instrument at each heating rate was determined by measuring the thermal lag observed for the melting of the Al wire.

Additionally, SDT experiments on Alex were carried out in helium and nitrogen. To avoid oxidation, the sample was purged with high flow rates of helium or nitrogen prior to the heating profile. Approximately 5.0 mg of sample and reference were heated at 5°C min^{-1} from 25 to 700°C in 100 mL min^{-1} carrier gas.

For the helium and nitrogen runs, the SDT was calibrated for TG mass, DTA baseline and temperature. The materials used for the temperature calibration were an indium SRM standard and high purity Al wire.

ARC

The ARC is a commercial automated adiabatic calorimeter distributed by Arthur D. Little Inc. and used for the purpose of assessing the thermal hazard potential of energetic materials [9]. Adiabatic conditions are maintained in this instrument, provided that the self-heating rate is less than about 10°C min^{-1}. Samples of about 0.5 or 1.0 g of Alex were placed in lightweight spherical titanium vessels (volume of 10 cm^3), which formed part of a closed system including a pressure transducer. A leak test of the system was performed at about 4.6 MPa prior to each experiment.

Experiments were started at both ambient pressure and 0.72 MPa of air. The standard ARC procedure of ‘heat-wait-search’ was used; the temperature of the system was raised from the initial temperature in 5°C steps at a heating rate of 0.5°C min^{-1}, the system was maintained adiabatic both during periods of ‘wait’ for dissipation of thermal transients and of ‘search’ for an exotherm defined as a self-heating rate (SHR) exceeding 0.02°C min^{-1}. The initial temperatures for the experiments on 0.5 and 1.0 g of Alex were 150 and 100°C respectively. The criteria set for the instrument to terminate a run were a temperature maximum of 400°C, a rate exceeding 1°C min^{-1} or pressure exceeding 3.45 MPa.

Results and discussion

Specific heat capacity

The specific heat capacities of nano and micron size Al powders were determined from the DSC measurements following the ASTM E1269 procedure [5]. The specific heat capacities obtained are the mean value for replicate determinations. In Fig. 1, the results are compared with literature values, which were determined using Outokumpu HSC Chemistry 3.0 and reference [10]. The specific heat capacities of the two Al powders between 30 and 400°C are similar. Their specific heat capacities increase significantly with temperature, and are different from the literature values for Al. These differences might be due to the impurity of the samples. It has been reported that Alex powder has an aluminium oxide coating thickness of 1.9 nm [2]. The specific heat capacity of aluminium oxide is higher and increases more rapidly with temperature than does that of pure aluminium; hence the nano and micron size Al powders have higher specific heat capacities due to the existence of this oxide layer.

Alex in air – kinetic parameters studies

Figure 2 shows the DTA and TG curves from SDT experiments in air at a heating rate of 5°C min^{-1}. An exotherm with an enthalpy change of 4.7±0.1 kJ g^{-1} was observed at a ‘true’ onset temperature of 481±5°C, where the ‘true’ onset temperature is the temperature at which a deflection from the established baseline is observed. The exotherm corresponds with a 21.9±0.4 % mass gain observed on the TG curve. The endotherm near 660°C is due to the melting of the unreacted Al core in the Alex particles. The results from the SDT experiments at different heating rates indicate that the mass gain for the exotherm and the enthalpy change for the melting endotherm are heating rate dependent. The lower the heating rate the higher the mass gain, and the enthalpy change for the melting endotherm is lower, since there is a smaller amount of unreacted aluminium. The reaction of Alex in air is a function of temperature and exposure time. The longer the sample was exposed to air after the onset temperature, the more the sample reacted. The enthalpy change for the exotherm likely decreases with increase in heating rate, but the difference is within the uncertainty limits (±0.1 kJ g^{-1}). After heating to 700°C, Alex did not agglomerate and its colour did not change.

The following description of the kinetic results is based on the n^{th} order rate law:

$$d\alpha/dt=k(1-\alpha)^n$$

and the Arrhenius equation

$$k=Ze^{(-E/RT)}$$

where α is the fraction of sample reacted ($0\leq\alpha\leq1$), k is the rate constant of the reaction, n is the order of the reaction, E is the activation energy and Z is the pre-exponential factor in the Arrhenius equation.

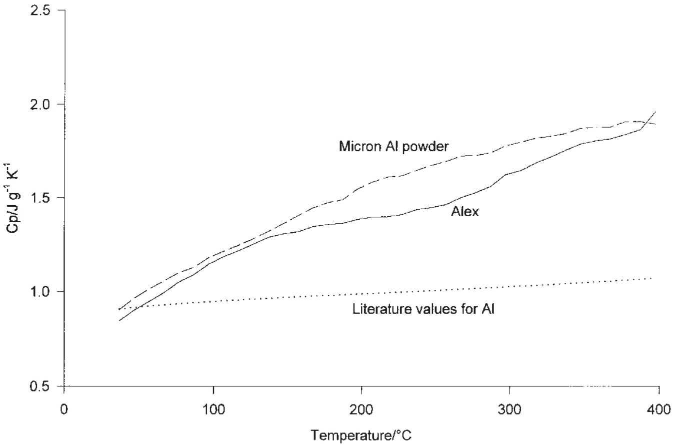

Fig. 1 Specific heat capacities of nano and micron size Al powders

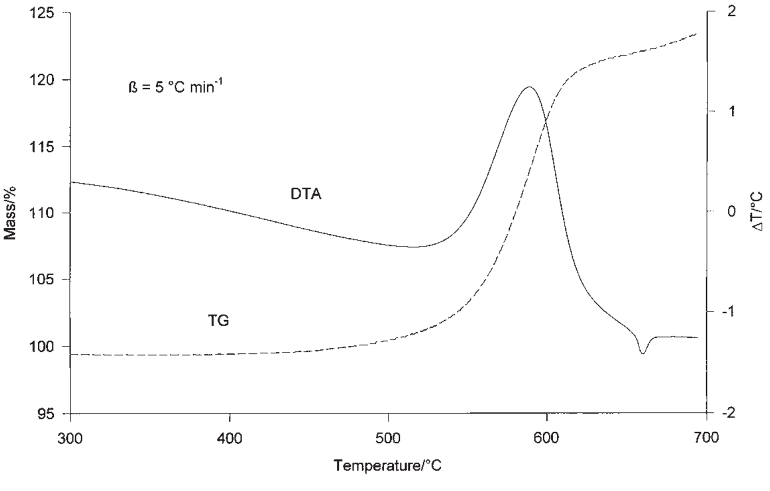

Fig. 2 SDT results for Alex in air at a heating rate of 5 °C min^{-1}

SDT

For the DTA results from the SDT experiments, in accordance with ASTM E698 method [7], the various heating rates were analyzed by plotting $\ln(\beta/T_m^2)$ *vs.* $1/T_m$, where β is the heating rate and T_m is the peak temperature, corrected for thermal lag. From the results depicted in Fig. 3, the quantities $E=225\pm3$ kJ mol^{-1} and $\ln(Z/\text{min}^{-1})=29\pm1$ were obtained.

From the TG measurements of the SDT experiments, Fig. 4 shows the plots of $\ln(\beta)$ *vs.* reciprocal temperature at 10, 15 and 20% conversions, in order to determine the kinetic parameters using the ASTM E1641 method [8]. Values of $E=211\pm10$ kJ mol^{-1} and $\ln(Z/\text{min}^{-1})=29\pm4$ were obtained at 15% conversion. The parameters obtained for the other conversions are shown in Table 1.

Table 1 Comparison of kinetics parameters for Alex in air by various methods

Methods		E/kJ mol^{-1}	$\ln(Z/\text{min}^{-1})$	n
DTA ASTM E698		225±3	29±1	(1.0)
TGA ASTM E1641	(10%)	206±15	29±3	(1.0)
	(15%)	211±10	29±4	(1.0)
	(20%)	219±7	31±4	(1.0)
TG Isothermal		215±9	28±2	1.2±0.1

( ) Assumption

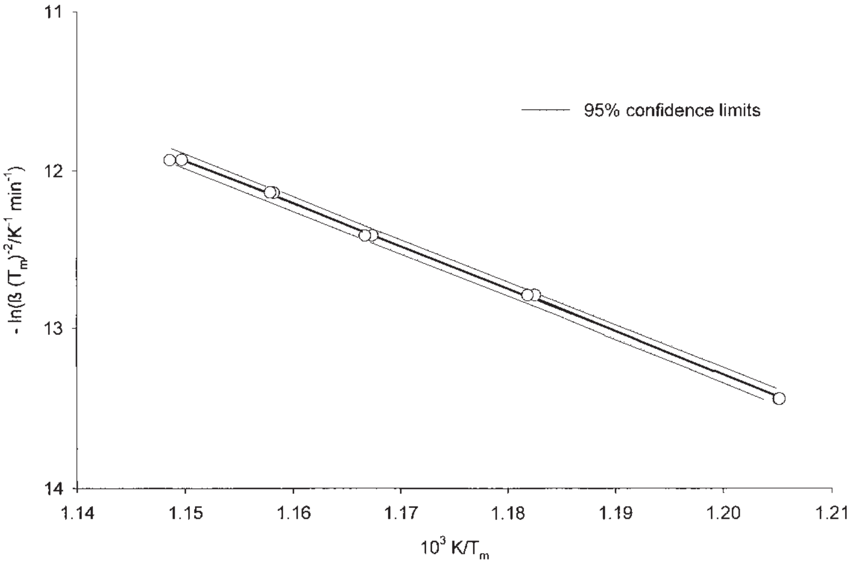

Fig. 3 Dynamic DTA studies for kinetic parameters

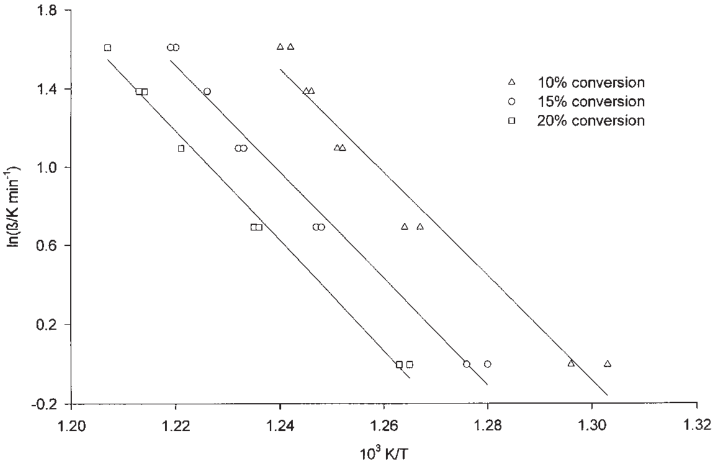

Fig. 4 Dynamic TG studies for kinetic parameters

TG

For the isothermal kinetic study conducted between 480 and 520°C, k and n were determined from a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $\ln(1-\alpha)$, where k is equal to the slope and n is the intercept of the plot. α was calculated from the mass% at time t and the extrapolated final mass gain. Figure 5 shows an example of this plot, the results were obtained at an isothermal temperature of 500°C. For all temperatures studied, a final mass gain of 25±2% was obtained. The kinetic parameters were determined from a plot of $\ln(k)$ *vs.* reciprocal isothermal temperature, as shown in Fig. 6. The slope of the straight line gives E and the intercept is $\ln(Z)$. Values of E=215±9 kJ mol^{-1}, $\ln(Z/\mathrm{min}^{-1})$=28±2 and n=1.2±0.1 were obtained.

The mass gain obtained from the isothermal TG data is higher than that from the SDT experiments at a heating rate of 5°C min^{-1} (21.9±0.4%), and it is closer to the value obtained from the experiments using a heating rate of 1°C min^{-1} (24.6±0.3%). This is due to the different duration of the experiments, as discussed in the previous section.

Alex in helium and nitrogen

Figure 7 shows the DSC results (using a heating rate of 0.5°C min^{-1}) for 5.0 mg of Alex in helium and nitrogen compared to the results in air. An additional run of 3.0 mg of Alex in nitrogen is also shown in Fig. 7. No reaction was detected in the helium environment. The results indicate that the oxidation process is detected at a lower temperature (439±5°C) than the nitridation. In nitrogen, different results were obtained when using different masses of the sample. A three-step exotherm with a ‘true’ onset temperature of 541±5°C was observed when using 5.0 mg of sample. The peak temperatures were 555±5, 557±5 and 574±5°C, with enthalpy changes of 3.5±0.3, 0.7±0.1 and 1.5±0.3 kJ g^{-1}, respectively for each peak. The enthalpy changes were estimated using PeakFit v4.0. For 3.0 mg of Alex, the exotherm was detected at 539±5°C in only one step with a peak temperature of 579±5°C and an enthalpy change of 5.9±0.4 kJ g^{-1}, in agreement with the total enthalpy change for the larger sample size.

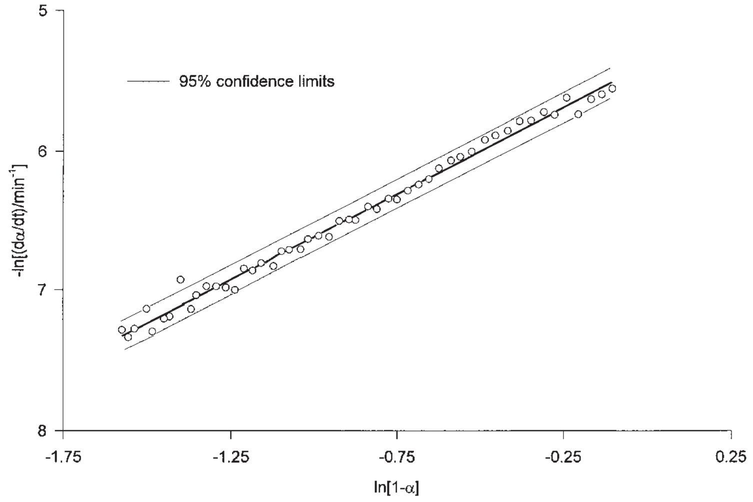

Fig. 5 Isothermal TG studies for kinetic parameters

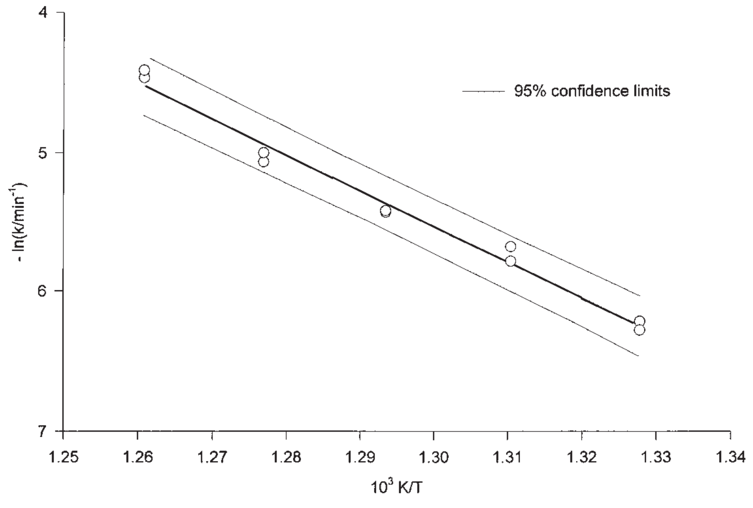

Fig. 6 Isothermal TG studies for kinetic parameters

As shown in Fig. 7, the onset temperatures of nitridation for both the 3.0 and 5.0 mg samples of Alex were similar, but the initial peak for the 5.0 mg sample of Alex occurred at a lower peak temperature. The results observed for the 5.0 mg sample may be due to a pressure effect. With a higher sample mass, there was less free headspace inside the pan. As the temperature increased, higher pressure developed in the headspace and a lower peak temperature was detected. When the amount of nitrogen inside the pan was depleted, pressure decreased, and nitridation was impeded. The DSC pan pin-hole then allowed pressure to build up again, further nitridation occurred, hence the third peak was observed.

An additional experiment was carried out using 5.0 mg of Alex without crimping the pans. A single step exotherm with a peak temperature of 588±5°C was ob-

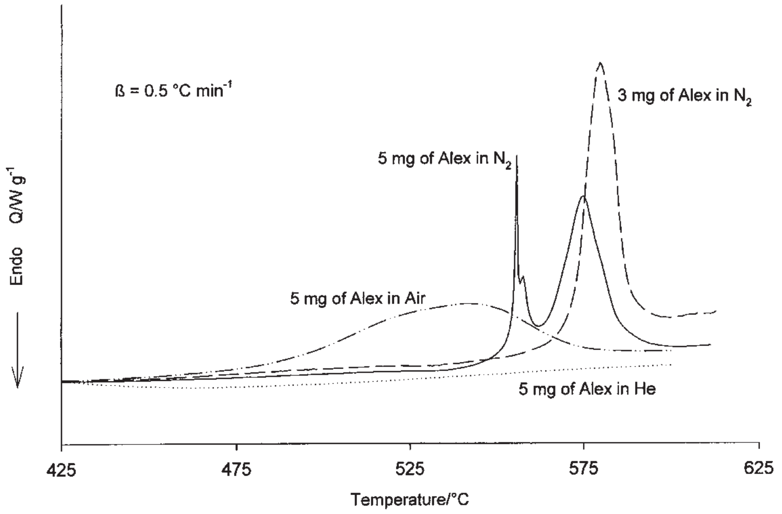

Fig. 7 DSC results for Alex in helium, nitrogen and air

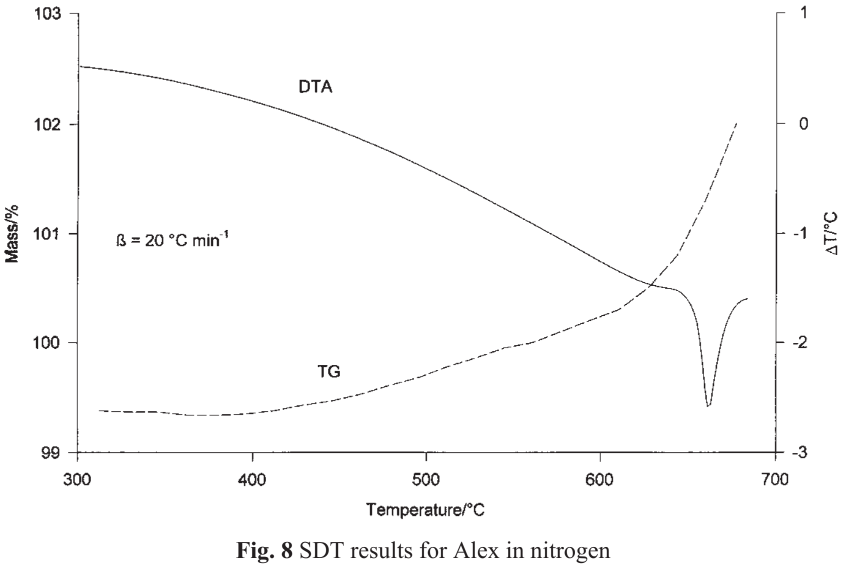

Fig. 8 SDT results for Alex in nitrogen

served, confirming that the occurrence of a multiple peak exotherm, with an initial, low peak temperature, may be due to a pressure effect.

Figure 8 shows that the exotherm was not detected when Alex was heated in nitrogen up to 680°C in the SDT. Note that the heating rate was 20°C min^{-1} for the SDT and 0.5°C min^{-1} for the DSC. The slow heating rate shifted the peak temperature to a lower value. Additionally, the SDT experiments were run in an open pan, but a hermetic pan with a laser-drilled pin-hole was used in the DSC experiments and a higher partial pressure of nitrogen in the pin-hole pan may have shifted the nitridation to a lower temperature.

ARC experiments

The conditions and results for ARC experiments are summarized in Table 2. The results for Alex experiments started at ambient air pressure are illustrated in Figs 9–10. The 1.0 g sample of Alex yielded three minor exotherms, followed by a large exotherm (exotherm defined as self-heating rate, SHR>0.02°C min^{-1}). The large exotherm had an ARC detected onset temperature of 340°C and continued until the run was stopped manually at 380°C (Fig. 9). For this exotherm, the ‘true’ onset temperature (extrapolated to SHR=0) was not determined, because the rate remained constant at 0.02°C min^{-1} as shown in Fig. 10. The pressure started to decrease near 340°C primarily due to oxidation of the Alex. No exotherm was detected using 0.5 g of Alex at ambient pressure of air, although a significant drop in pressure was observed.

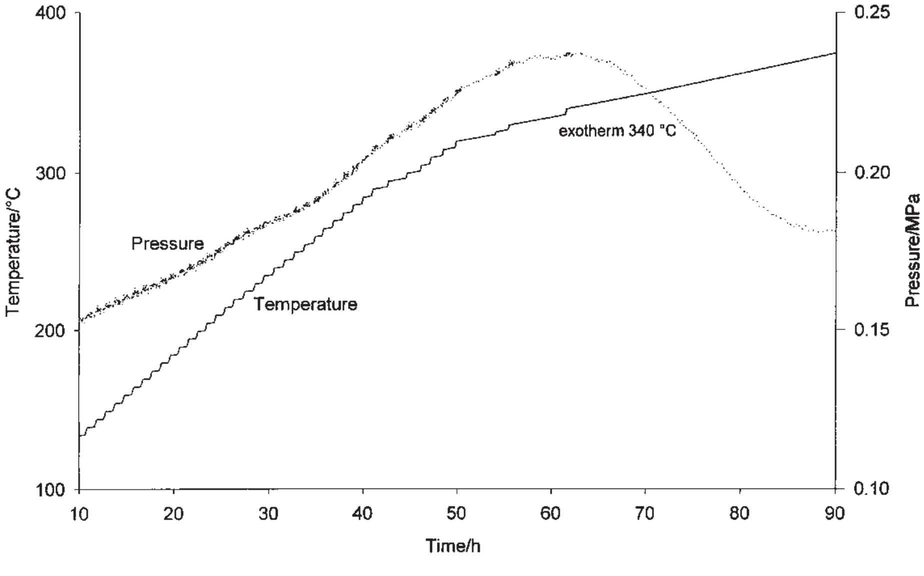

Fig. 9 ARC results for 1.0 g of Alex at ambient pressure

Table 2 Comparison of ARC results for Alex in air

Run #	1	2	3
Mass/g	1.0038	0.5068	1.0029
Mass gain/mg	1.5	2.3	12.8
Mass gain/%	0.15	0.45	1.28
Start T/°C	100	150	100
End T/°C	378	286	350
Initial P/MPa @ T_{initial}/°C	0.11 16	0.72 22	0.72 26
End P/MPa @ T_{final}/°C	0.11 31	0.68 23	0.54 26

In Figs 10–12, the results of experiments starting at 0.72 MPa of air are shown. Several minor exotherms were observed. For the run started at 150°C with 0.5 g of Alex, a large exotherm was detected from 255°C until the run was stopped manually at 286°C (Fig. 11). As shown in Fig. 10, the rate remained constant for this large exotherm and the 'true' onset temperature could not be determined. This large exotherm was not observed in the run of 1.0 g of Alex started at 100°C (Fig. 12), where the pressure started to decrease near 265°C and to increase again at 315°C. Although no large exotherm was observed, the decrease in pressure, which corresponds with the depletion of oxygen (and possibly nitrogen) indicates a reaction of Alex. The mass gain obtained after the run was 12.8 mg, which is larger than the values obtained from the other runs (Table 2), also suggesting that a reaction occurred. However, when comparing the mass gain obtained and the predicted mass gain for complete oxidation (0.447 and 0.894 g for 0.5 and 1.0 g of Alex, respectively, assuming the sample is pure Al), the results show that the oxidation was not complete. The amounts of oxygen contained in the system were 2.74 and 19.4 mg for experiments started at ambient pressure and 0.72 MPa of air, respectively. In both cases, there was insufficient oxygen for complete oxidation. However, the mass gains obtained were smaller than predicted from the original amounts of oxygen in the system. Hence, some oxygen remained in the system after the run and oxidation was not solely limited by the amount of oxygen available. Additionally, nitridation of Alex did not likely occur, because the DSC results (Fig. 7) show that oxidation of Alex occurred at a lower temperature.

Comparison of results

For the reaction of Alex in air, the kinetic parameters determined using different methods are compared in Table 1. There is good agreement between the isothermal TG, dynamic DTA and TG results, considering the uncertainties in these results. No literature values are available for comparison.

For the ARC results, the exotherms or the decline in pressure indicated oxidation of Alex. The onset temperatures were 340 and 255°C for experiments started at ambient pressure and at 0.72 MPa, respectively. From DSC and DTA results, the 'true' onset temperatures for the reaction were 439 and 481°C, respectively. It appears that the differences in the results are, at least partially, caused by significant variations in experimental conditions, such as the nature of the system, sample size, heating rate, pressure, etc.

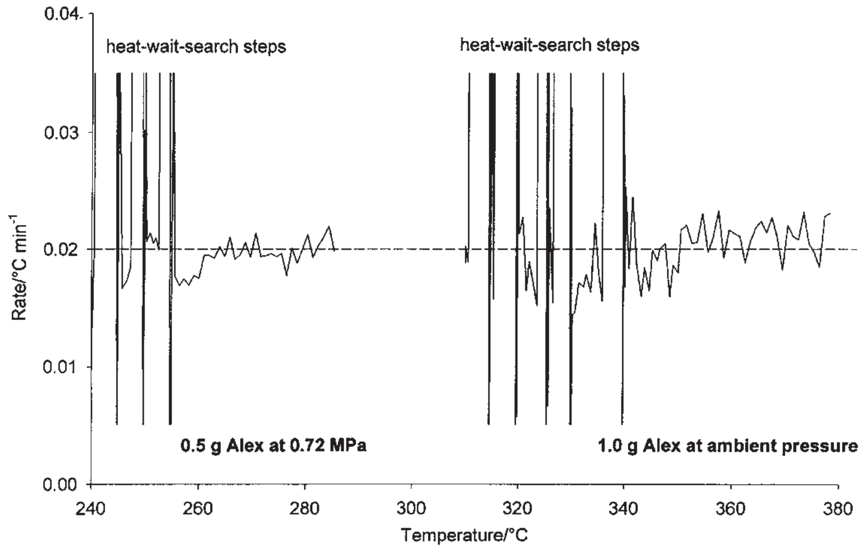

Fig. 10 Rate *vs.* temperature graphs for ARC results

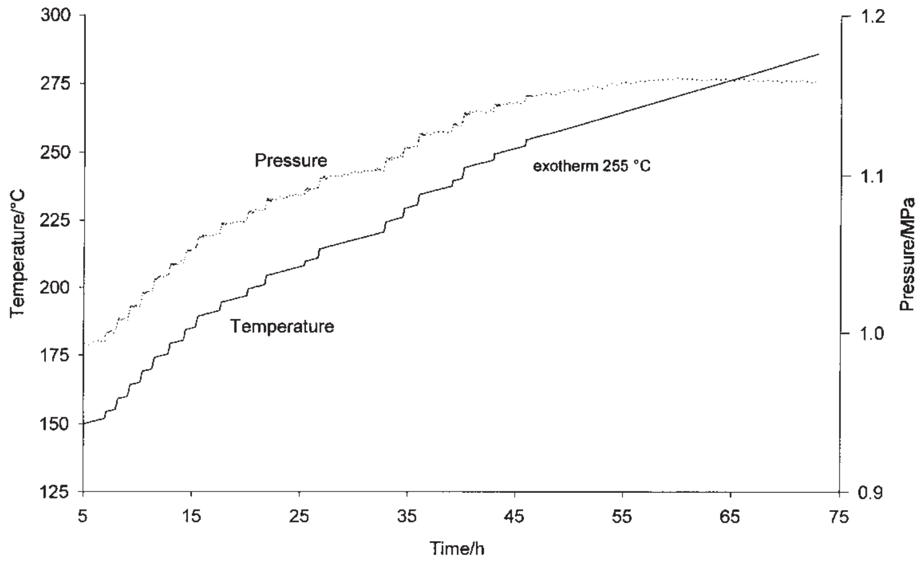

Fig. 11 ARC results for 0.5 g of Alex at 0.72 MPa

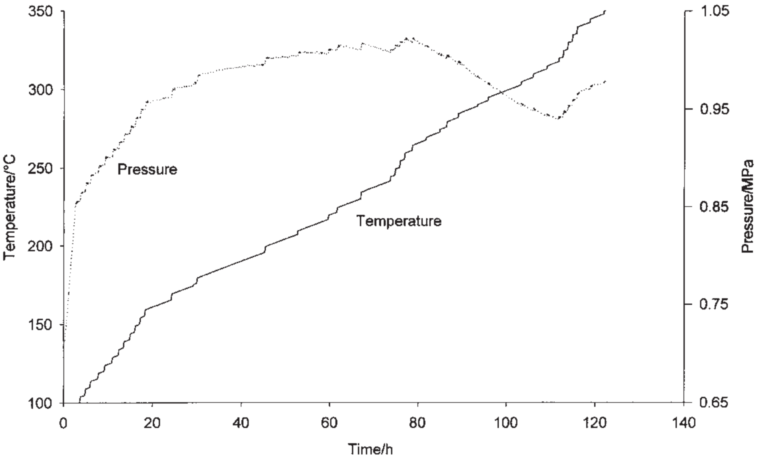

Fig. 12 ARC results for 1.0 g of Alex at 0.72 MPa

Conclusions

The ASTM technique for heat capacity gives reliable results for Al nano and micron size powder. Their specific heat capacities were similar between 30 and 400°C, but different from the literature values for aluminium due to the existence of the oxide coating.

The thermal behaviour of Alex in nitrogen, helium and air was evaluated. An exotherm was observed near 540°C from the DSC results for Alex in nitrogen when using a vented hermetic pan. No exothermic events were detected in helium. The SDT experiments in air indicated that there was an exotherm at an onset temperature of 481±5°C with an enthalpy change of 4.7±0.1 kJ g^{-1}. The kinetic parameters for the reaction of Alex in air, determined using different methods, are in good agreement.

For the ARC experiments, several exotherms were detected between 150 and 350°C at ambient pressure and 0.72 MPa of air. The results showed that the pressure started to decrease at 340 and 260°C for experiments started at ambient pressure and at 0.72 MPa, respectively.

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