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Short communication

The influence of alumina passivation on nano-Al/Teflon reactions

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ABSTRACT

The reaction kinetics of aluminum (Al) and polytetrafluoroethylene (PTFE or Teflon) were recently examined using nanoparticles of both Al and Teflon. Results showed a unique pre-ignition reaction (PIR) associated with the nano-Al/Teflon mixture that was not significant in the micron-Al/Teflon mixture. The PIR is caused by fluorination of the alumina (Al_2O_3) shell passivating the Al particles and reduces the onset temperature of Al ignition for nano compared with micron particle mixtures. Because the alumina shell was found to play a key role in the reaction mechanism, this communication extends our understanding of the interaction between alumina and Teflon by examining the influence of alumina particle size, and therefore surface area, on the fluorination reaction with Teflon. Differential scanning calorimetry analysis show that reaction kinetics vary dramatically as the alumina particle size is reduced from 50 to 15 nm diameter. Specifically, for 15 nm diameter alumina, the first exotherm (corresponding to the PIR) exhibits three times more heat of reaction than for the 30, 40, or 50 nm alumina particles. These results show how particle size and specific surface area affect the Al–Teflon reaction mechanism.

1 Experimental

In order to determine the effects of increased surface area on the reaction between alumina and Teflon thermal analysis was conducted using a Netzsch STA 409 PC Luxx differential scanning calorimeter/thermogravimetric analyzer (DSC/TGA). In order to isolate the effects of increased surface area from changes in composite properties caused by differing sample composition all samples were prepared using the same mass ratio of 34% Teflon to 66% alumina.

Samples were prepared in a manner identical to that described in [1]. All samples were mixed in batches of 100 mg, with 34 mg Teflon and 66 mg of alumina. The Teflon particle size was held constant at 200 nm for all tests. The alumina particle size was varied from test to test to change the surface area ratio of alumina to Teflon. Specific surface areas were calculated from the particle's density and average diameter. All particles have a spherical morphology and further information is shown in Table 1.

Between 2 and 3 mg of powder mixture was loaded into a Pt crucible with an alumina liner. The powder was slightly compressed in the crucible to insure good thermal contact. The crucible was then placed into the DSC/TGA and a turbo pump was used to evacuate the DSC/TGA to a vacuum of at least 1.0×10^{-4} mbar. Once this vacuum was achieved the DSC/TGA was backfilled with argon to atmospheric pressure and a constant argon purge was established with a flow rate of 59.5 ml/min. The sample was then heated from 25 to 750 °C at 20 degrees per minute.

2 Results

Fig. 1 shows the heat flow curves as a function of temperature for alumina–Teflon mixtures with alumina particle size ranging from 15 to 50 nm diameters. For alumina particles greater than 30 nm three exotherms are present with onset temperatures for the first exotherm increasing with decreasing particle size (Table 2). This trend implies that as particle size decreases, the first two exotherms appear to merge toward each other with the onset temperature increasing from 371.1 °C for 50 nm diameter to 418.2 °C for 15 nm diameter. The third exotherm has an onset temperature between 550 and 558 °C and exhibits the greatest heat release.

For the 15 nm alumina–Teflon mixture the reaction kinetics are limited to two exotherms. The 418.2 °C onset temperature of the first exotherm is delayed 45 °C and exhibits three times more energy than the larger alumina particle mixtures. The onset of the exotherm corresponding to the maximum heat release for the 15 nm alumina mixture is reduced by 50 °C from the larger particle mixtures and occurs at 506 °C.

It is noted that for the 15 nm alumina mixture limited exothermic behavior may be occurring before the endotherm. Further supporting evidence for this is that the endotherm is significantly smaller than that for the other samples suggesting that the exothermic and endothermic behaviors are happening simultaneously. Confirmation of this activity at slower heating rates could not be resolved; however, Fig. 1 suggests the possibility of reaction kinetics

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Table 1
Alumina and Teflon powder property data.

Material	Manufacturer	Particle size (nm)	Specific surface area (m^2/g)	Alumina/PTFE surface area ratio
Teflon	DuPont	200	13.64	N/A
Alumina	Nanotechnologies, Inc.	15	100.76	7.39
Alumina	Nanotechnologies, Inc.	30	50.38	3.69
Alumina	Nanotechnologies, Inc.	40	37.78	2.77
Alumina	Sigma–Aldrich	50	30.23	2.22

Table 2
Tabulated DSC data for each mixture of alumina and Teflon.

	Onset temperature		Energy of reaction	
Alumina diameter	1st exotherm (°C)	Final exotherm (°C)	1st exotherm (J/g)	Final exotherm (J/g)
15 nm	418.2	506.9	35.89	306.55
30 nm	398	558.5	10.52	188.21
40 nm	380.9	553.9	11.18	174.78
50 nm	371.7	549.9	12.26	348.18

associated with the 15 nm alumina mixture at temperatures below and/or coinciding with Teflon melting (i.e., 320 °C).

3 Discussion

In recent work [1] it was suggested that for nm Al particles reacting with a fluoropolymer such as Teflon, delaying the onset temperature of the fluoropolymer decomposition to temperatures approaching the ignition of nm Al (roughly 600 °C) would promote a more complete and efficient overall reaction. Results from Fig. 1 suggest that one way to manipulate the decomposition onset temperature of Teflon is with the alumina surface area. Osborne and Pantoya [1] showed the PIR for the nano-Al and Teflon mixtures starts at 400 °C and corresponds with the first exotherm observed in all curves in Fig. 1. The three times higher heat of reaction in the first exotherm for the 15 nm alumina case may also promote the PIR. The exothermic peak associated with the AlF_3 transition from β to α phase has been documented to occur at roughly 550 °C [2] and corresponds with the exotherms with the highest heat of reaction in Fig. 1. As particle size reduces, this exotherm shifts toward lower onset temperatures which may also promote the Al–Teflon reaction by creating more heat release at temperatures closer to the PIR thereby facilitating aluminum fluorination.

Relating these observations directly to the Al–Teflon reaction implies that for alumina passivated Al particles, the smallest particles with highest specific surface area will promote ignition and reaction by: (1) delaying the onset temperature of Teflon decomposition to higher temperatures more closely approaching the ignition temperature of nm Al particles; (2) exhibiting higher exothermic behavior in the first exotherm corresponding to the pre-ignition reaction; and (3) reducing the onset temperature for the β to α phase transition of AlF_3.

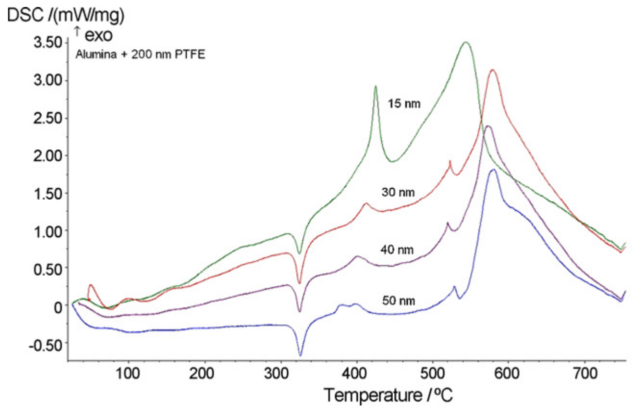

Fig. 1. Heat flow curves for alumina–Teflon reactions as a function of alumina particle diameter.

A literature review on the thermochemistry of the reactants indicates that the first endotherm observed in Fig. 1 for all samples is consistent with Teflon melting (i.e., 320 °C) [1,3]. Teflon experiences endothermic evaporation/decomposition beginning at 520 °C as observed in [1,2]. Alumina is initially amorphous but undergoes several phase changes upon heating such that transitions to γ-Al_2O_3 are conceivable at temperatures below 600 °C [4]. The magnitudes of these endothermic phase changes are not significantly detectable with the DSC at 20 degrees per minute heating rates; however, can be observed in TG data presented in [4]. The exothermic behaviors observed in Fig. 1 are therefore a consequence of alumina/fluorpolymer reactions and not phase changes of the reactants.

4 Conclusions

These results show that the reaction kinetics associated with the extraction of fluorine from Teflon and the subsequent formation of AlF_3 are a strong function of the alumina particle diameter. As the surface area increases (i.e., for alumina particles 15 nm in diameter) the number of exotherms merge from three into two that correspond with the absorption of fluoride ions from Teflon that start reacting at 400 °C to form alumino–fluoro complexes such as β-AlF_3 which transition phase from β to α at 550 °C. These results imply that higher surface area interaction between the alumina passivation on Al particles and Teflon will delay Teflon decomposition to temperatures approaching the nm Al ignition temperature and promote greater exothermicity in the PIR which has been shown to facilitate the Al–Teflon reaction.

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