Quasi-static mechanical behaviors of different inert particle reinforced Al/PTFE reactive composites

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Abstract. In this paper, the quasi-static mechanical behaviors of particle reinforced aluminum/polytetrafluoroethylene (Al/PTFE) reactive composites are studied. The mechanical behaviors of composites with the volume fraction of 30% W, WC, SiC and SiO₂ respectively are compared by the quasi-static compression test, and the failure mechanism is analyzed. Test results show that SiC/SiO₂ particle reinforced composites show better toughness, while W/WC particle reinforced composites show more brittleness. The failure mechanism analysis indicates that the failure of particle reinforced composites is mainly caused by matrix fracture and particle spalling from the matrix.

1. Introduction
As a new class of reactive material, fluoropolymer-based material has been widely studied by a large number of scholars for its high energy and unique reaction characteristics, and has been applied to missile warhead as a reactive damage fragments to enhance the damage effect. Among them, PTFE/Al, as a typical representative of fluoropolymer-based energetic materials, has the characteristics of metal-like strength, dynamite-like energy and relative insensitivity, and has become a research and application focus [1].

In recent years, researches on the properties of PTFE/Al reactive material mainly include mechanics and energy release performance. Reftenberg [2] studied the mechanical properties of PTFE/Al materials by quasi-static compression and SHPB test, and determined the Johnson-Cook (JC) model. Casem [3] preformed compression tests to analyze the mechanical properties of PTFE/Al materials, including a discussion of the strain rates of loads and a discussion of the temperatures of materials. According to the experiments, the parameters for both JC and the Modified Johnson-Cook (MJC) constitutive models were generated. The mechanical properties of PTFE/Al have a significant direct impact on its reaction properties. Ames [4] performed the chamber experiments to investigate energy release characteristics of PTFE/Al and discussed the impact-induced reaction mechanism. It was shown that the reaction of PTFE/Al materials starts from the strong shear region under the impact of high strain rate. Feng [5] performed the drop-weight tests to study the mechanical sensitivity of
PTFE/Al with different Al particle size and sintering temperature under low-speed impact. Test results showed that crack-induced ignition was the main control mechanism under low-speed impact.

Numerous studies have shown that mechanical properties of materials can be effectively improved by adding appropriate amount of particulate matter to polymer-based materials. At present, researches mainly focus on adding W particles, as an inert component, to PTFE/Al reactive material system to improve the strength and density of materials. The quasi-static compression test showed that the failure stress of the material increases with the increase of W content, but the toughness decreases [6]. Cai [7] conducted the drop-weight test to discuss the effect of property of W on PTFE/Al/W material. Test results showed that the strength of composite with porous small W particles is higher than that of composite with dense large W particle. Ge [8] investigated the mechanical property of brittle PTFE/Al/W with a low temperature sintering process. Test results indicated that the toughness of material decreases with the increase of W content, as well as PTFE/Al/W material with a high temperature sintering process.

However, there are little researches about other inert particle reinforced PTFE/Al material except PTFE/Al/W material. In order to investigate the effect of particle type on the mechanical reinforcement of the PTFE/Al reactive material system, four series of particle reinforced PTFE/Al composites, with different inert particles as W, WC, SiC and SiO$_2$, were prepared in this paper. Among them, W and WC as high density inert particles, can effectively improve the material density, while SiC and SiO$_2$ as typical ceramic powders, are widely used in mechanical reinforcement of other material systems. The mechanical properties of PTFE/Al series materials strengthened by the above four particles were compared by the quasi-static compression test, and the relationship between particle reinforcement effect and particle type was analyzed.

2. Experimental setup

2.1. Simple preparation

In this paper, four inert particle reinforced reactive composites were prepared, and 30% inert particles were added to PTFE/Al zero-oxygen equilibrium system. The added inert particles were W, WC, SiC and SiO$_2$, with an average size of 20 μm. Raw materials: PTFE powder (average particle size: 24 μm, density: 2.2 g·cm$^{-3}$, from 3F, Shanghai, China); Al powder (average particle size: 24 μm, density: 2.78 g·cm$^{-3}$, from XRY, Beijing, China); W powder (average particle size: 20 μm, density: 19.35 g·cm$^{-3}$, from PingYuan, Hebei, China); WC powder (average particle size: 20 μm, density: 15.63 g·cm$^{-3}$, from PingYuan, Hebei, China); SiC powder (average particle size: 20 μm, density: 3.2 g·cm$^{-3}$, from PingYuan, Hebei, China); SiO$_2$ powder (average particle size: 20 μm, density: 2.6 g·cm$^{-3}$, from PingYuan, Hebei, China). When the PTFE/Al/inert particle reactive composite is impacted, the main reactions would occur as shown in equations (1).

$$4\text{Al}+3\text{C}_2\text{F}_4 \rightarrow 4\text{AlF}_3 + 6\text{C} + 8670\text{kJ}$$  \(1\)

As shown in the equation, the reaction volume ratio of PTFE/Al material is 77.4:22.6. According to the above proportion, a certain amount of PTFE, Al and inert particle powder is taken as mixed powder, which is prepared into a Φ10mm×10mm sample through two processing methods, namely cold isostatic pressing (CIPing) followed by high-temperature sintering (HTSing) in a vacuum
sintering oven. The pressing pressure was about 250MPa. In the sintering process, the oven temperature was risen up to 360℃ at 60℃/h, and then keep at 360℃ for 4 hours. Lastly, the specimens cooling to room temperature at 60℃/h, as shown in the figure 1. The information of all kinds of samples is listed in table 1. All kinds of typical samples are shown in figure 2. For each kind of reactive composites, three samples were tested to reduce consistency errors.

Table 1. The parameters of the typical samples.

| Type | Component | Content(vol.%) | $\rho^a$ (g·cm$^{-3}$) | $\rho^b$ (g·cm$^{-3}$) | Relative density | Sintered |
|------|-----------|----------------|------------------------|------------------------|------------------|----------|
| A1   | PTFE/Al/W | 54.2/15.8/30.0 | 7.437                  | 6.102                  | 0.820            | NO       |
| A2   | PTFE/Al/W | 54.2/15.8/30.0 | 7.437                  | 5.404                  | 0.727            | YES      |
| B1   | PTFE/Al/WC| 54.2/15.8/30.0 | 6.321                  | 5.206                  | 0.824            | NO       |
| B2   | PTFE/Al/WC| 54.2/15.8/30.0 | 6.321                  | 4.047                  | 0.640            | YES      |
| C1   | PTFE/Al/SiC| 54.2/15.8/30.0 | 2.592                  | 2.562                  | 0.988            | NO       |
| C2   | PTFE/Al/SiC| 54.2/15.8/30.0 | 2.592                  | 2.408                  | 0.929            | YES      |
| D1   | PTFE/Al/SiO₂| 54.2/15.8/30.0 | 2.412                  | 2.372                  | 0.983            | NO       |
| D2   | PTFE/Al/SiO₂| 54.2/15.8/30.0 | 2.412                  | 2.267                  | 0.940            | YES      |

$^a$ $\rho^a$ represents theoretical maximum density.

$^b$ $\rho^b$ represents the actual density.

**Figure 1.** Temperature in the vacuum sintering oven.

**Figure 2.** Typical samples of different inert particle reinforced composites.
As shown in table 1, when the cold isostatic pressing at a same pressure, the relative density \(\rho_a/\rho_t\) of samples with different inert particles was significantly different. For unsintered samples, the relative density of samples with W and WC particles is about 0.82, while the relative density of samples with SiC and SiO\(_2\) particles is about 0.98. After sintering, the relative density of samples all decreased, among which the relative density of samples with WC particles decreased the most. The above phenomena indicate that particle properties have significant influence on the internal microstructure of composites. The binding between high density particles, such as W and WC, and PTFE matrix is weaker than that between low density particles, such as SiC and SiO\(_2\), and PTFE matrix.

2.2. Methods

The quasi-static compression experiments which were about sample with different inert particle was performed by the WDT series Universal Materials Testing Machine controlled by a computer. Schematic of the compression experimental setup is shown in figure 3, where \(D_0\) and \(H_0\) are the initial diameter and height of the sample, respectively. The compression speed of cross-head was 0.6mm/min, corresponding to an approximate strain rate of \(10^{-3}/s\).

![Figure 3. Schematic of the compression experimental setup.](image)

In order to reduce the friction between the ends of the sample and the equipment in the compression test, the ends of the sample were coated with Vaseline for lubrication. Three samples were tested at each type to examine the reproducibility of test results. According to the recorded by testing machine, the engineering stress and engineering strain of samples could be calculated by equation (2).

\[
\begin{align*}
\sigma_e &= \frac{P}{A_0} \\
\varepsilon_e &= \frac{H_0 - H}{H_0}
\end{align*}
\]

Where \(\sigma_e\) and \(\varepsilon_e\) are the engineering stress and engineering strain, \(P\) is the pressure of the sample during the compression test, \(A_0\) and \(H_0\) are the initial cross-sectional area and height of the sample, \(H\) is the height of the sample during the compression test, respectively. Based on material incompressibility theory, the true stress and true strain could be expressed as equation (3).
\[
\begin{align*}
\sigma &= \frac{P}{A_0}(1 - \varepsilon) \\
\varepsilon &= \ln \frac{1}{1 - \varepsilon}
\end{align*}
\]

Where \( \sigma \) and \( \varepsilon \) are the true stress and true strain, respectively. The true stress-strain curve is usually used to analyze the mechanical properties of samples.

3. Results and discussion

3.1. Failure morphology and mechanism

Figure 4 presents the failure behavior of the unsintered samples with different inert particles under the quasi-static compression. As shown in the figure, there are significant difference among samples with different inert particles of crack morphology. There are axial crack and inclined crack on the cylindrical surface of type A1 sample (PTFE/Al/W). The crack of type B1 (PTFE/Al/WC) begin at the end then axial extension following tilt extension. The cracks of type C1 and D1 samples (PTFE/Al/SiC and PTFE/Al/SiO\(_2\)) are 45° inclined cracks. The above phenomena indicate that the mechanical properties of different particle reinforced PTFE/Al reactive composites show significant differences.

![Figure 4](image1.png)

Figure 4. Typical failure behavior of sample: (a) type A1, (b) type B1, (c) type C1, (d) type D1.

Figure 5 presents the failure behavior of sintered samples with different inert particles under quasi-static compression. As shown in the figure, when the engineering strain is 0.3, type A2 and B2 samples have axial cracks. It was not until strain 0.7 that the type C2 sample cracked at the edge. When the engineering strain is 0.7, type D2 sample remains thin and round, without any cracks. It is worth noting that the B2 samples form a conical core at a certain angle when the strain is relatively large, and the periphery has an axial fracture.

![Figure 5](image2.png)

Figure 5. Typical failure behavior of sample: (a) type A2, (b) type B2, (c) type C2, (d) type D2.

The failure of the sample is mainly caused by PTFE matrix fracturing or particles spalling from
PTFE matrix. Before sintering, the particles and the PTFE matrix in the sample only interact under physical mix, which are in a relatively loose state. In the heating process, PTFE starts to melt and get into a viscoelastic state of a certain liquid formation when it is higher than 327 °C. So, PTFE matrix can flow freely within a certain area and fill the internal gap in the sample. In the cooling process, recrystallized PTFE turns into the overall structure and improves the integrity of the base. Sintering process enhances the strength between the substrate on one hand, and strengthen the substrate to the parcel of particles on the other hand. Therefore, sintered samples have significantly higher strength than unsintered ones.

Although sintered samples with W or WC particles have higher strength than unsintered ones, they still show significant brittleness. Contrary to this, sintered samples with SiC and SiO$_2$ particles show better toughness. This indicates that the particle characteristics have great influence on the sintering process of samples. On one hand, it may be caused by the different liquidity of viscoelastic state PTFE on the surface of the different particles, which is determined by the molecular structure of the particles and PTFE matrix and make the matrix to package and combining with the particles. Test results show that the liquidity of PTFE on the surface of the SiC and SiO$_2$ particles is better than that on the surface of the W and WC. On the other hand, the sintering state of samples differs due to the difference in heat conduction characteristics of particles.

It is noted that the experiments of type A2 is different from the experimental results in reference [6], which indicate that the sintered PTFE/Al/W samples show good toughness. The reason for this difference can be explained as follows: In reference [6], the sintering temperature of PTFE/Al/W reached 380°C, while in this paper, the sintering temperature was only 360°C. Due to the low sintering temperature, the PTFE matrix has a low fluidity and cannot tightly wrap W particles, which reduces the mechanical strength of the sample and causes brittle fracture in a certain degree. Moreover, this difference also implies that the mechanical properties of materials are influenced by the coupling of particle type and sintering temperature. When the particles are added into PTFE/Al reactive materials, higher sintering temperature is needed to increase the fluidity of viscoelastic PTFE on the particle surface and improve the encapsulation degree of PTFE matrix on the particles, so that the particle reinforced composites would show higher toughness.

3.2. mechanical responses

The type of added inert particles has important effect on the mechanical properties of particle reinforced composites. The true stress-strain curve of unsintered PTFE/Al with different types of inert particles is shown in figure 6 and 7 respectively. On the whole, the true stress-strain curve of unsintered samples has a similar trend, including the elastic stage, the plastic stage and the failure stage. Under the quasi-static compression, the sample first occurs elastic deformation, and the true stress increases linearly with true strain. Then the material starts to yield and occurs plastic deformation. After a certain degree of plastic deformation, the true stress decreases with the increase of true strain after reaching the yield stress, when the material enters the failure stage. All kinds of inert particle reinforced composites show good consistency before failure but great difference after failure. The reason is, relatively stable internal force chain in the sample make the material mechanics response show good consistency before failure. But the internal force chain ruptures and rearranges with great randomness when compressing the failure sample, which results in the great difference of
stress-strain curve of the failed samples made of the same material.

![Stress-strain curves](image)

**Figure 6.** The true stress varies with true strain: (a) type A1, (b) type B1, (c) type C1, (d) type D1.

![Comparison of stress-strain curves](image)

**Figure 7.** The comparison of true stress-strain curve among A1, B1, C1, and D1.

According to the stress-strain curve of each type of sample in figure 6 and figure 7, the static mechanical property parameters of each type of composites can be obtained and listed in table 2. As shown in table 2, the elastic modulus of the composite decreases successively in order of type A1
(PTFE/Al/W), type C1 (PTFE/Al/SiC), type B1 (PTFE/Al/WC) and type D1 (PTFE/Al/SiO₂). In general, the type of particles has little influence on the elastic modulus of the particle reinforced composites. However, it has a great influence on the yield strength. The yield strength of type A1 (16.43MPa), which is the highest among four types of composites is 1.90 times that of type D1 (8.67MPa) which is the lowest among four types of composites. This indicates that adding W particles improves the resilience of deformation under the compression. In the aspect of failure stress, type A1 has the highest failure stress and type B1 has the lowest failure stress, while type C1 and type D1 have basically the same failure stress which is just a little lower than that of type A1. This indicates that W particle has the most significant strength reinforcement effect on PTFE/Al reactive materials. In the aspect of failure stress, type C1 has the highest failure strain and type B1 has the lowest failure strain. This indicates that SiC particles have the most significant toughness reinforcement effect on PTFE/Al reactive materials. In general, mechanical properties of type A1 and type C1 are better than those of the other two composites. W particles are conducive to improving the strength of the composite, and SiC particles are conducive to improving the toughness of the composite, indicating that the mechanical reinforcement effect of particle reinforced PTFE/Al composites can be significantly affected by the properties of particle added.

| Type | Elasticity modulus (MPa) | Yield stress (MPa) | Average failure stress (MPa) | Average failure strain |
|------|-------------------------|-------------------|-------------------------------|-----------------------|
| A1   | 773.44                  | 16.43             | 22.55                         | 0.0645                |
| B1   | 659.61                  | 14.38             | 18.97                         | 0.0601                |
| C1   | 718.43                  | 14.00             | 21.49                         | 0.0889                |
| D1   | 603.11                  | 8.67              | 21.75                         | 0.0759                |

The true stress-strain curve of sintered different particle reinforced PTFE/Al reactive composites is shown in figure 8 and 9. As shown in the figure, there is a huge difference between the true stress-strain curve of the sintered or unsintered samples. For sintered samples, there are only elastic and plastic stage, but no failure stage basically. The elastic response of each sintered sample is similar to unsintered one, when the stress increases linearly with the strain. In the elastic stage, the stress of type A2 (PTFE/Al/W) basically does not change, possibly because the particles undergo rearrangement after the rupture of the internal force chain of the sample and form a stable force chain again. The stress of type B2 (PTFE/Al/WC) increases with strain at a lower rate in the plastic section than that in the elastic stage. When the strain exceeds 0.4, the stress increases rapidly with strain. The mechanical response of type C2 (PTFE/Al/SiC) and D2 (PTFE/Al/SiO₂) is basically similar in the plastic stage, and the stress increases with strain at a higher rate than that of type A2 and B2. When the strain exceeds 0.4, the stress of all samples increases rapidly with the strain.
4. Conclusion
The mechanical properties of particle reinforced PTFE/Al reactive composites with W, WC, SiC, and SiO$_2$ in volume fraction of 30%, were investigated by quasi-static compression. The quasi-static
mechanical response behavior and failure mode of these materials are strongly dependent on the type of particles added into the PTFE/Al reactive materials. The following conclusions can be drawn as follows:

- Under the same molding stress, the relative density of materials depends on the type of added particles. The relative density of PTFE/Al composites with W or WC particles was only 0.64 to 0.824, but the relative density of PTFE/Al composites with SiC or SiO₂ particles was as high as 0.929 to 0.989.
- Unsintered particle reinforced PTFE/Al composites show brittleness, but the mechanical properties of the material, including failure stress and failure strain, are different. The failure stress of composites with W particles is the highest, while the failure strain of composites with SiC particles is the highest. After sintering, the strength of samples increased significantly. The strength of samples with W or WC particles was lower than that with SiC or SiO₂ particles. The maximum failure stress was obtained by adding W particles, and the maximum failure strain was obtained by adding SiC.
- The failure mode of composites is strongly dependent on the type of particles, among which, the composites with SiO₂ particles are the most ductile, and the composites with WC particles are the most brittle.

Reference
[1] Wang H, Zheng Y, Yu Q, Liu Z and Yu W 2011 J. Appl. Phys. 110 074904
[2] Raftenberg M, Mock W and Kirby G 2008 Int. J. Impact Eng. 35 1735–44
[3] Casem D 2008 Mechanical response of an Al-PTFE composite to uniaxial compression over a range of strain rates and temperatures Army Research Laboratory Report
[4] Ames R 2005 43rd AIAA Aerospace Sciences Meeting and Exhibit 10–13 January Reno Nevada 279
[5] Feng B, Qiu C, Zhang T, Hu Y, Li H and Xu B 2019 Propellants Explos. Pyrotech. 44 630-6
[6] Xu F, Liu S, Zheng Y, Y Q and Wang H 2017 Adv. Eng. Mater. 19
[7] Cai J, Nesterenko V, Vecchio K, Jiang F, Herbold E, Benson D, Addiss J, Walley S and Proud W 2008 Appl. Phys. Lett. 92
[8] Ge C, Wubuliaisam M, Dong Y and Tian C 2017 Materials 10