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ARTICLE

Effects of Al and W Particle Size on Combustion Characteristics and Dynamic Response of W-PTFE-Al Composites

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Abstract: The variation of metallic particle size alters the combustion characteristics and dynamic response of W-PTFE-Al composites. Combustion test results show that with Al particle size decreasing from 10 μm to 1 μm, W particle size increasing from 0.1 μm to 7 μm, the reaction energy of W(7 μm)-PTFE(40 μm)-Al(1 μm) reaches 4570.2 J/g in argon environment and 9848.1J/g in oxygen environment, indicating fine aluminum and coarse tungsten contribute to the increase of reaction energy. Under dynamic loading, the deflagration time of all four kinds of W-PTFE-Al composites is longer than 500 μs. With the decrease of Al particle size, the insensitivity of W-PTFE-Al composites to impact shows a decreasing tendency since the absorbed critical energy before reaction decreases by 14.0%. With the decrease of W particles size, the insensitivity of W-PTFE-Al composites to impact enhances due to the absorbed critical energy before reaction increases by 34.8%. The dynamic compression results show that the ultimate strength of W-PTFE-Al composites increases by 8.0% with Al particle size changing from 10 μm to 1 μm, but decreases by 10.2% with W particle size changing from 7 μm to 100 nm.

Key words: composite materials; combustion characteristic; insensitivity; dynamic response

Aluminum (Al)-Polytetrafluoroethylene (PTFE) is a typical kind of reactive materials, which undergo severe exothermic reactions or explosion under dynamic loading[1,2]. In recent years, this kind of materials have received broad attention due to the special response to dynamic loading[3].

The major research orientations contain composition ratios, surface modification, additives and particle size. As for composition ratios, the stoichiometric ratio for reaction is 26.5%Al:73.5%PTFE by weight. And Zhao et al[4] investigated the dynamic compression properties of Al-PTFE reactive materials with different composition ratios and the results indicates that the ultimate strength shows an increasing tendency with the increased content of Al. Moreover, the content of Al should not be more than 35 wt% or it may result in incomplete combustion due to insufficient oxidizing agent (PTFE). This result is vital in designing the composition ratio of Al-PTFE composites. Songlin Xu et al[5] investigated the effects of different Al contents of Al-PTFE on mechanical performance and the results show that the tensile strength reaches the highest level when the Al content is 6%. In addition, the damage behavior of Al-PTFE includes three steps, which is the 1st deformation, the 2nd ductile cracks and the 3rd exothermic reaction. As for surface modification, Brown[6] investigated the effect of mechanical activation of high specific surface area aluminum with PTFE on composite solid propellant and found the beginning reaction temperature of activated Al-PTFE powder is lower than that observed with non-activated Al-PTFE powder but the burning rate increases due to the large specific surface of the activated aluminum. However, the low density and low strength of Al-PTFE composites severely restrict the application of this kind of material. In order to solve this problem, some researchers try

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to add additives into Al-PTFE composites. One potential way is to add tungsten (W) to Al-PTFE composite. In our previous work[7], W was added in Al-PTFE composites with different mass ratios and the result shows that with the increase of W content from 50% to 80%, both the density and strength increase obviously while the reaction energy still remains in high level. In this paper, 50 wt%W was added to improve density and mechanical properties of Al-PTFE. The high density of W results in that its actual volume ratio in W-PTFE-Al (mass ratio: 50%W, 35%PTFE and 15%Al) is only 10.6%, which will not severely decrease the reaction energy of PTFE-Al. As for particle size of W, Nesterenko et al.[8] investigated the mechanical properties of W-PTFE-Al composites with different W particle sizes and the results show that reducing W particle size contributes to the increase of ultimate compressive strength. Cai et al.[9] observed the samples of W-PTFE-Al composites after compressed at the strain rate of 4×10^2 s^{-1} and found severe plastic deformation occurs in PTFE by forming nanofiber structure. However, researches have been mainly focused on the mechanical properties of W-PTFE-Al composites with different particle sizes. There are few literatures related to the effect of particle size on the combustion characteristics and dynamic response which is of great significance when using as reactive materials.

This paper aims at demonstrating the effects of different Al and W particle sizes on combustion characteristics and dynamic response to impact of W-PTFE-Al composites.

1 Experiment

The W-PTFE-Al composites have the following average particle size as shown in Table 1. And the mass ratio of W-PTFE-Al composites is 50%W, 35%PTFE, and 15%Al. The particle size of PTFE remains unchanged because in our previous work, reducing the particle size of PTFE will make it unable to form continuous PTFE matrix after sintering and thus severely weaken the mechanical property. The process of preparing W-PTFE-Al composite included powder mixing, cold isostatic pressing (CIP) and vacuum sintering. The CIP process and sintering process are shown in detail in our previous work[6]. Fig.1 shows the microstructures of W-PTFE-Al composites. It can be seen that both Al particles and W particles are homogenously distributed in a PTFE matrix in sample 1#, 2# and 3#. However, in sample 4#, severe agglomerations of W nanoparticles occur (SEM morphology). Both the densities and relative densities increase with Al particle size change from 10 μm to 1 μm but decrease with W particle size change from 7 μm to 100 nm as shown in Table 2. This phenomenon indicates that samples with fine Al particles propel densification compared with samples with coarse Al particles. However, samples with fine W particles resist densification compared with samples with coarse W particles.

Table 1 Particle size of four types of W-PTFE-Al composites (μm)

Sample No.	Al particle size	W particle size	PTFE particle size
1#	10	7	40
2#	5	7	40
3#	1	7	40
4#	1	0.1	40

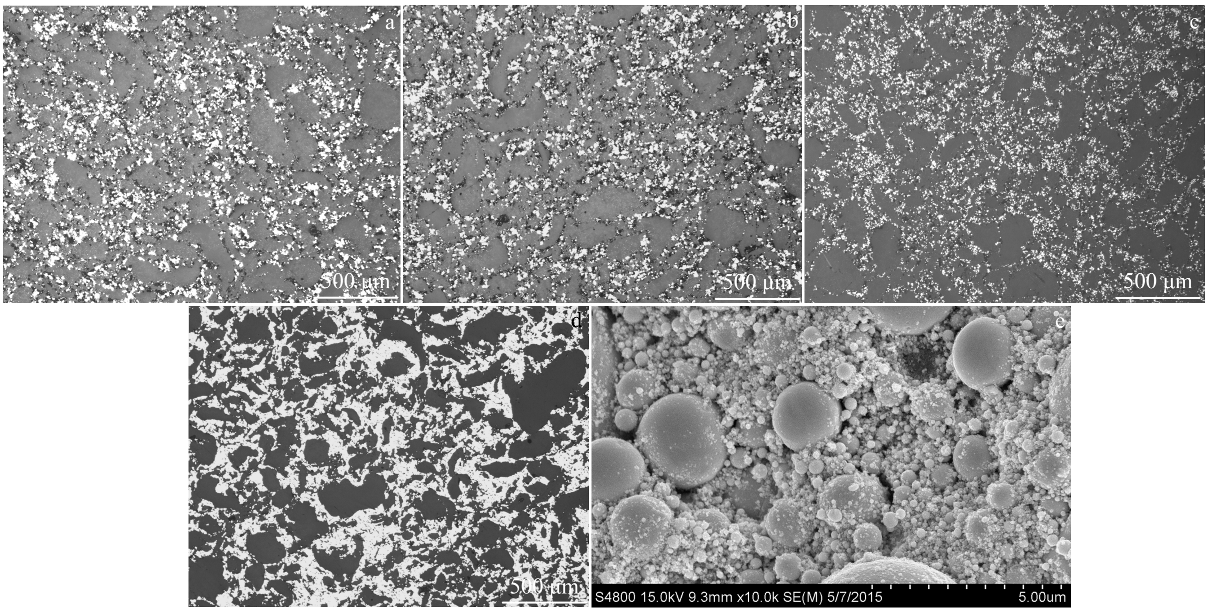

Fig.1 Microstructures of four kinds of W-PTFE-Al composites: (a) sample 1#: W(7 μm)-PTFE(40 μm)-Al(10 μm); (b) sample 2#: W(7 μm)-PTFE(40 μm)-Al(5 μm); (c) sample 3#: W(7 μm)-PTFE(40 μm)-Al(1 μm); (d) sample 4#: W(0.1 μm)-PTFE(40 μm)-Al(1 μm); (e) SEM morphology of sample 4#

Table 2 Densities of W-PTFE-Al composites

W-PTFE-Al composite	Density/g·cm^{-3}	Relative density/%
1#	3.94	95.9
2#	3.98	96.8
3#	4.03	98.1
4#	3.79	92.2

Calorimeter (Parr 6200) was used to test the reaction energy of four kinds of powders in oxygen and argon environment. Then the solid products after ignition were analyzed by XRD.

To reveal the dynamic response of W-PTFE-Al composites to impact, specimens were impacted by split Hopkinson pressure bar (SHPB) and the size of specimen is Φ5 mm×3 mm. High-speed photography was performed to record the behavior of W-PTFE-Al composites to impact. Then the absorbed critical energy before reaction can be calculated by the formula:

$$E = \int_{\varepsilon_0}^{\varepsilon_f} \sigma \mathrm{d}\varepsilon \qquad (1)$$

in which ε_0 represents the strain of the yielding point and ε_f represents the strain of the reaction starting point[6].

In order to analyze the quasi-static and dynamic mechanical property of W-PTFE-Al composites, cylindrical samples (Φ10 mm×10 mm) were tested by CMT4305 universal materials machine at the strain rate of 10^{-3} s^{-1} and SHPB at the strain rate of 10^3 s^{-1}.

2 Results and Discussion

2.1 Combustion characteristics

The combustion results are shown in Table 3. In argon atmosphere, the reaction energy of W-PTFE-Al composites increases by 13.3% with Al particle size decreasing from 10 μm to 1 μm. However, the reaction energy of W-PTFE-Al composites decreases by 17.9% with W particle size decreasing from 7 μm to 100 nm. And in oxygen atmosphere, the reaction energy of W-PTFE-Al composites increases by 4.6% with Al particle size decreasing from 10 μm to 1 μm. But, the reaction energy decreases by 12.7% with W particle size decreasing from 7 μm to 100 nm. This result indicates that fine Al particle can be helpful in increasing reaction energy of W-PTFE-Al composites while fine W particle plays a negative role in reaction energy of W-PTFE-Al composites. Moreover, the reaction energy of W-PTFE-Al composites in oxygen atmosphere is much higher than that of W-PTFE-Al composites in argon atmosphere. This phenomenon indicates that oxygen contributes to the reaction of W-PTFE-Al composites.

Fig.2 shows the XRD patterns of W-PTFE-Al composites after ignited in oxygen atmosphere. The final reaction products in four kinds of W-PTFE-Al composites are identified to be AlF_3, WO_3 and C. The presence of AlF_3 indicates that Al is oxidized by fluorine from the PTFE. Besides, the presence of WO_3 from the reaction between W and O_2 at high temperature, indicates W also participates in the exothermic reaction in oxygen atmosphere.

2.2 Dynamic response to impact

Under impact loading (strain rate 5900~6200 s^{-1}), all samples react vigorously, as shown in Fig.3. The deflagration time of all kinds of W-PTFE-Al composites lasts for 500 μs. From the reaction images it can be seen that when Al particle size decreases, the initial time to impact is kept in 350 μs. However, when W particle size decreases, the initial time to impact delays from 350 μs to 400 μs. Comparing images of samples under high strain rate loading reveal that the reaction severity of W-PTFE-Al composites shows an increasing tendency with the decreasing of Al particle size; however, with the decreasing of W particle size, the reaction severity of W-PTFE-Al composites shows a decreasing tendency.

From the true stress-time curves in Fig.4a, the true stress can be determined by the initial time point and thus the corresponding initial point in the true stress-strain curves, as shown in Fig.4b, can be determined. Then the absorbed critical energy before reaction of sample 1#, 2#, 3#, and 4# is calculated, which are 307.7, 299.7, 274.5 and 356.6 J/cm^3 respectively. It can be seen that the absorbed critical energy before reaction decreases by 14.0% with Al particle size changing from 10 μm to 1 μm. However, the absorbed energy increases by 34.8% with W particle size changing from 7 μm to 100 nm. This phenomenon is due to fine Al particles increase the total interface area between metallic particles and PTFE, which weakens the insensitivity to impact of composites. But, severe agglomerations of W nanoparticles decrease the total interface area between metallic particles and PTFE, which enhances the insensitivity to impact of composites.

The remnants of four kinds of W-PTFE-Al composites after impact are shown in Fig.5. It is found that the reaction

Table 3 Reaction energy results of W-PTFE-Al (J·g^{-1})

Atmosphere	1#	2#	3#	4#
Ar	4033.3	4410.7	4570.2	3750.7
O_2	9411.3	9696.3	9848.1	8600.9

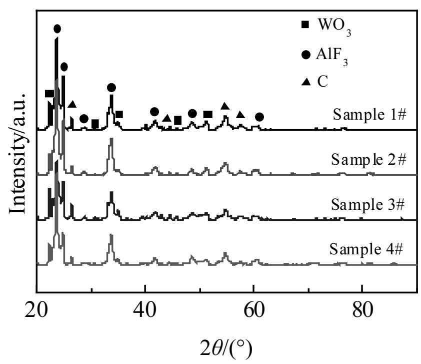

Fig.2 XRD patterns of W-PTFE-Al composites after ignited in oxygen atmosphere

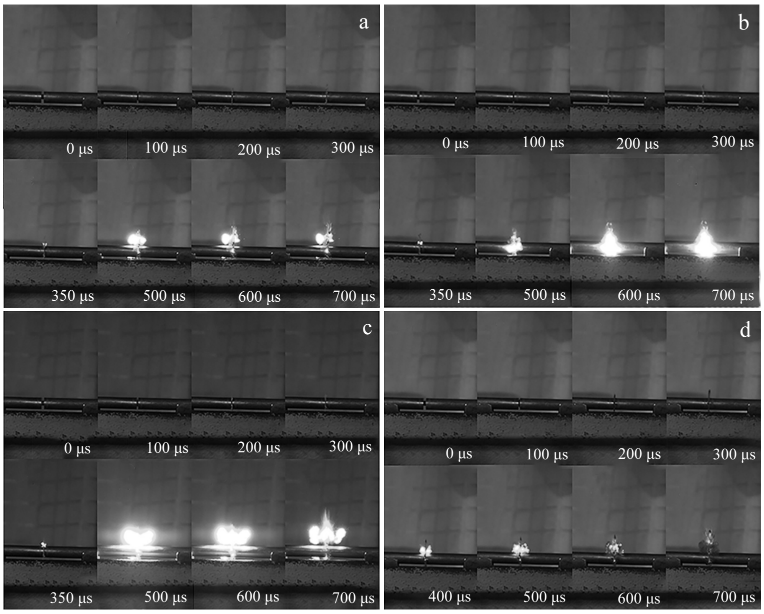

Fig.3 Pictures of W-PTFE-Al composites under impact loading: (a) sample 1#: W(7 μm)-PTFE(40 μm)-Al(10 μm); (b) sample 2#: W(7 μm)-PTFE(40 μm)-Al(5 μm); (c) sample 3#: W(7 μm)-PTFE(40 μm)-Al(1 μm); (d) sample 4#: W(100 nm)-PTFE(40 μm)-Al(1 μm). Impact occurs at 0 μs

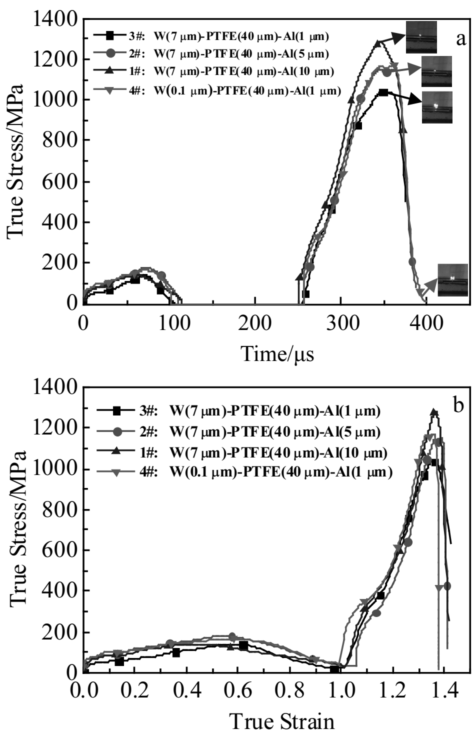

Fig.4 Hopkinson bar test results of four W-PTFE-Al composites: (a) true stress-time curves and (b) true stress-true strain curves

completeness shows an increasing tendency with decreased Al particle size. However, the reaction completeness shows a decreasing tendency with decreased W particle size. W(7 μm)-PTFE(40 μm)-Al(1 μm) shows the highest reaction completeness.

By analyzing the initial time to impact loading, reaction severity, the absorbed critical energy before reaction and reactive completeness of composites, it can be concluded that the insensitivity to impact of W-PTFE-Al composites shows a decreasing tendency with decreased Al particle size but exhibits an increasing tendency with decreased W particle size.

2.3 Quasi-static and dynamic compression properties

Fig.6a shows the true stress-strain curves of all four kinds of W-PTFE-Al composites obtained from the quasi-static compression test. The degree of strain hardening effect is obviously different for all four kinds of W-PTFE-Al composites. With the decreasing of Al particle size, the strain hardening effect shows an increasing tendency. However, with decreased W particle size, the strain hardening effect shows an obviously decreasing tendency which can be attributed to the agglomerations of W particles. Among all four kinds of composites, sample 3# shows the strongest strain hardening effect, indicating that reducing Al particle size and increasing W particle size contribute to improving mechanical property. Moreover, no failure occurs of all composites which indicates good ductility.

Fig.6b shows the true stress-strain curves of four kinds of W-PTFE-Al composites obtained by SHPB. The corresponding compressive strengths of samples 1#, 2#, 3# and 4# are 100, 106, 108 and 97 MPa, respectively. The critical failure strain (approximately 0.30) shows little change among all four kinds of composites. It can be seen that the ultimate

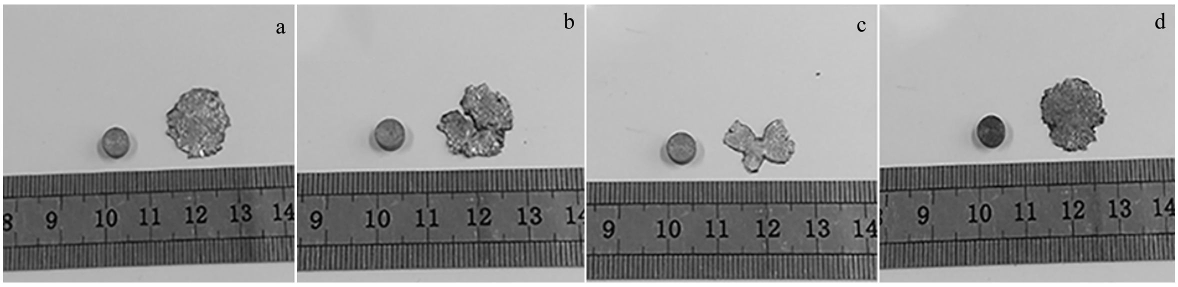

Fig.5 Retrieved solid remnants of W-PTFE-Al composites after ignition: (a) sample 1#, (b) sample 2#, (c) sample 3#, and (d) sample 4#

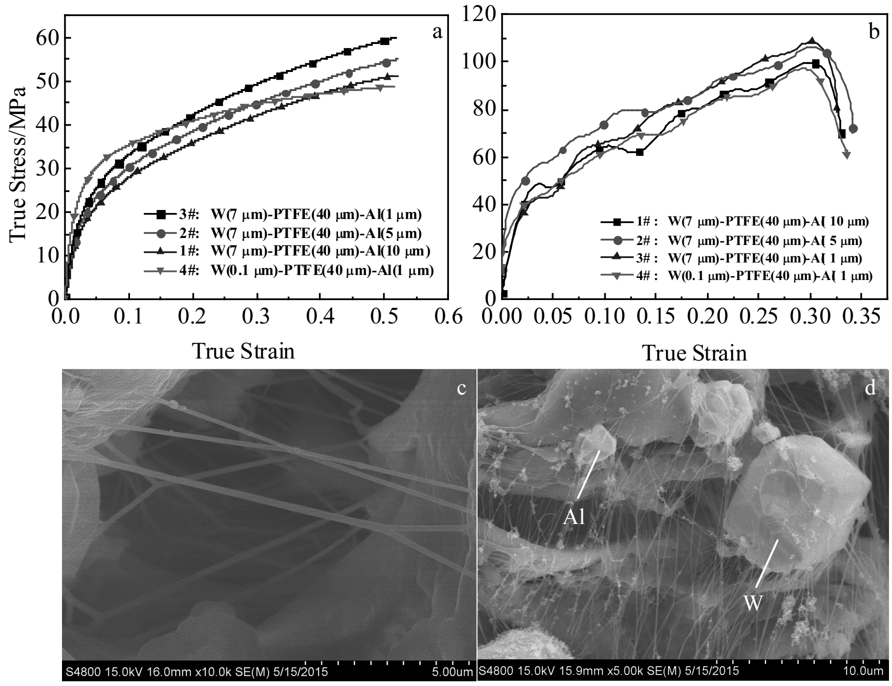

Fig.6 True stress-strain curves (a, b) and microstructure (c, d) of W-PTFE-Al composite after impact: (a) true stress-strain curves under quasi-static loading (strain rate 10^{-3} s^{-1}), (b) true stress-strain curves under dynamic loading (strain rate 2300~2450 s^{-1}), (c) nanofiber of PTFE in W-PTFE-Al composites after impact, and (d) undeformed W and undeformed Al in W-PTFE-Al composites after impact

strength of W-PTFE-Al composites increases by 8% with Al particle size decreasing from 10 μm to 1 μm. This result can be attributed to the improvement of densification and better interface bonding. However, the ultimate strength of composite decreases by 10.2% with W particle size changing from 7 μm to 100 nm. Coupled with the microstructure of sample 4# in Fig.1d and Fig.1e, agglomerations of W nanoparticles are responsible for this decrease of the strength of the composites. The unchanged critical failure strain of all four kinds of composites can be attributed to the facts that plastic deformation mainly concentrates on PTFE, which is a decisive factor to the critical failure strain while both W particles and Al particles show little deformation as shown in Fig.6c and 6d. In addition, obvious strain hardening effect can be seen in true stress-strain curves of all four kinds of W-PTFE-Al composites.

3 Conclusions

1) The reaction energy of W-PTFE-Al composites in both argon and oxygen atmosphere increases with Al particle size changing from 10 μm to 1 μm but decreases with W particle size changing from 7 μm to 100 nm, indicating fine Al particle can be helpful in enhancing reaction energy of W-PTFE-Al composites while fine W particle plays a negative role in enhancing reaction energy of W-PTFE-Al composites.

2) Under impact loading (strain rate 5900~6200 s^{-1}), the dynamic response of composites with different particle sizes varies obviously. The insensitivity of W-PTFE-Al composites to impact shows a decreasing tendency with decreased Al particle size but exhibits an increasing tendency with decreased W particle size according to the absorbed critical energy before reaction.

3) Under dynamic compression loading, the ultimate strength of W-PTFE-Al composites increases by 8% with Al particle size decreasing from 10 μm to 1 μm, which can be attributed to the improvement of densification and better interface bonding. However, the ultimate strength decreases by 10.2% with W particle size decreasing from 7 μm to 100 nm which is due to the severe agglomerations of W nano-particles. The critical failure strain remains unchanged among all composites which can be attributed to the fact that plastic deformation of composite mainly concentrates on PTFE.

4) The influence of Al particle size can be attributed to the characteristics of densification as well as the change of total interface area between metallic particle and PTFE. The influence of W particle can be attributed to agglomerations of W particles, which will change the total interface area between metallic particle and PTFE.

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铝粉和钨粉粒径对 W-PTFE-Al 复合材料燃烧特性和动态响应的影响

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摘　要：通过调控金属粉末的粒径可以显著改变 W-PTFE-Al 复合材料的燃烧特性和动态响应。燃烧性能测试结果表明，随着铝粉粒径从 10 μm 降至 1 μm，钨粉粒径从 0.1 μm 升至 7 μm，W(7 μm)-PTFE(40 μm)-Al(1 μm)复合材料在氩气气氛下的反应能量为 4570.2 J/g，在氧气气氛下反应能量为 9848.1 J/g。这表明减小铝粉粒径和增大钨粉粒径有助于 W-PTFE-Al 复合材料反应能量值的提高。在冲击条件下，4 种 W-PTFE-Al 复合材料燃烧时间均超过 500 μs。随着铝粉粒径的减小，反应临界吸收功降低 14%，“钝感”特性呈现下降趋势。随着钨粉粒径的减小，反应临界吸收功升高 34.8%，“钝感”特性呈现上升趋势。动态压缩试验结果表明，随着铝粉粒径从 10 μm 降至 1 μm，W-PTFE-Al 复合材料的抗压强度提高 8.0%；随着钨粉粒径从 7 μm 降至 100 nm，W-PTFE-Al 复合材料的抗压强度降低 10.2%。

关键词：复合材料；燃烧特性；钝感；动态响应

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