Properties of Ultrafine Aluminum Powders Modified by Facile Grafting with Glycidyl Azide Polymer

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Abstract：The ultrafine aluminum powders with diameter of $1-2$ μm were surface grafted by energetic glycidyl azide polymer（GAP）using diisocyanate as bridge via consecutive condensation reactions between —OH and —N＝C＝O groups. The surface properties, compatibility with fluorine polymeric binders as well as resistance to water oxidation of the prepared GAP-grafted aluminium powders were studied. Results show that the static water contact angle of surface of aluminum powders before and after grafting is $0-25.7°$ and $109.9°$, respectively. The surface property of aluminum powders is changed from hydrophilic to hydrophobic after surface grafting. The GAP grafted aluminum powders have better compatibility with fluorine polymeric binders. Moreover, The stability tests for aluminum powders were conducted in water at 70 ℃. 39.8%（mass fraction）of active aluminum are oxidized after 15 min, for the untreated fresh aluminium powders. Only 1.4% of active aluminum are oxidized after 60 min for GAP-grafted aluminum powders, revealing that grafting with GAP can effectively protect the aluminum powders under harsh hydrothermal conditions.
Key words：energetic materials；ultrafine aluminium powders；glycidyl azide polymer（GAP）；surface grafting
CLC number：TJ55；O62   **Document code**：A   **DOI**：10.11943/j.issn.1006-9941.2015.08.020

1 Introduction

Aluminum powders are widely used as additive in the field of energetic materials [1-3], due to its unique high calorific value and low cost. The application of ultra fine aluminum powders is always limited by（1）the agglomeration due to its high surface energy and strong particle interaction [4];（2）easily oxidized by water [5-6];（3）low compatibility with polymeric binders [7].

To address these problems, various approaches have been developed for the processing of aluminum powders [8-10]. Dave et al [11] studied the flowability of spherical aluminum powders processed by coating nano-particles of silica, titania and carbon black and promethyltrichlorosilane. Alexander Gromov et al [12] coated aluminum powders with nitrocellulose, oleic acid and stearic acid, which were suspended in kerosene and ethanol, amorphous boron, nickel, fluoropolymer, ethanol and air. Among these approaches, coating with oleic acid in ethanol showed best efficiency to protect aluminum from being oxidation, however, large amount of aluminum powders treated by oleic acid were still reacted during the aging test（after 50 min, over 30%（mass fraction）aluminum were consumed）. Krasnoperov et al [13] coated aluminum powder with diameter of 30 μm with PVDF in super critical carbon dioxide, and aging test showed that it moderately protected the aluminum powders in aqueous solution（after 70 minutes, about 37% alumi-num was consumed）. These results indicate

that physical coating is not well-proportional and the interaction between coating materials and aluminum particles is weak, which can not efficiently protect aluminum powders in high humidity. Besides physical coating, chemical grafting is another attractive route to coat aluminum powders with protective shells [14-17]. Charles Dubois et al [16] grafted 18% PE and 12% polyurethane onto 120 nm aluminum powders, aging test in water at 60 ℃ showed that it provided effective way to protect aluminum powders. However, grafting with large amount of passivative materials might bring problem to the energy releasing efficiency of aluminum powders in the application of energetic materials [18]. Recently, Anderson et al [18] reported that the type of binders（energetic or non-energetic）could have apparent effect on the early reaction of aluminum in the pressed aluminized explosives. GAP is unique energetic polymer with a heat of formation of $+490.7$ kJ·mol^{-1} [19]. The terminated hydroxyl groups of GAP polymers can offer some convenient reactions, e.g. efficient reaction with —N＝C＝O group. On the other hand, there are hydroxyl groups on the surface of aluminum powders [16-17]. Therefore, GAP molecular can be grafted to the aluminum powders with diisocyanate as bridge via consecutive condensation reactions between —OH and —N＝C＝O groups.

In this paper, we report studies on the method of ultra fine aluminum powders with diameter of $1-2$ μm treated by surface grafting with GAP polymers and the surface properties, compatibility with fluorine polymeric binders as well as the water oxidation-resistance ability of the GAP-grafted aluminium powders.

2 Experimental

2.1 Materials

Aluminumpowders with diameter of $1-2$ μm were bought from Yuhong nano tech.（Guangzhou, China）. It was dried for 10h under vacuum before use. The active aluminum content of the aluminum powders is 99.8%. Acetonitrile was pu-

rified by CaH_2 followed by distillation and used in fresh. Ditin butyl dilaurate (DBTDL, 95% solution) was purchased from Aladdin (Shanghai, China). Toluene-2, 4-diisocyanate (TDI, 99%) was bought from Xiya agent (Chengdu, China). Glycidyl azide polymer (GAP) was kindly given from Liming Chemical Engineering Institute (Luoyang, China). The molar mass distribution of GAP was characterized by using gel permeation chromatography (Agilent GPC50). The conventional universal calibration with linear polystyrene standards was used. The elution agent used was THF and the flow rate was kept at $1.0 \ mL \cdot min^{-1}$. The molecular mass (M_n) of GAP was 3600 $g \cdot mol^{-1}$, where the polydispersity index (M_w/M_n) was 1.6. Other reagents were used without further purification unless noted otherwise.

2.2 Methods

Surface grafting on aluminumpowders was conducted by using consecutive condensation reaction between —OH and —N＝C＝O groups, as shown in Fig. 1. For a typical experiment, 5 g aluminum powders were dispersed in a flask with 50 mL acetonitrile assisted with ultrasonic processing. 0.6 g DBTDL was added to the flask under vigorous stirring in the presence of argon gas inlet. 4 g TDI was added to the flask and the mixture was stirred for 2 h at 80 ℃ oil bath. Then the mixture was cooled down to room temperature, filtered and washed with acetonitrile. And then the mixture was transferred to a flask and dispersed in 50 mL acetonitrile. 0.6 g DBTDL was added to the flask under vigorous stirring in the presence of argon gas inlet. Then 5 g GAP was added to the flask and the reaction mixture was stirred for 2 h at 80 ℃ oil bath. Then the mixture was cooled down to room temperature, filtered and washed with acetonitrile for 5 times. The products were dried in vacuum for 12 h and the GAP-grafted aluminum powders were obtained. The grafting amount of GAP on the aluminum powders determined by TG/DSC curve (in N_2 atmosphere) was 1.3%, corresponding to the mass loss from 200 ℃ to 550 ℃, which was due to the exothermic decomposition of GAP molecular[20].
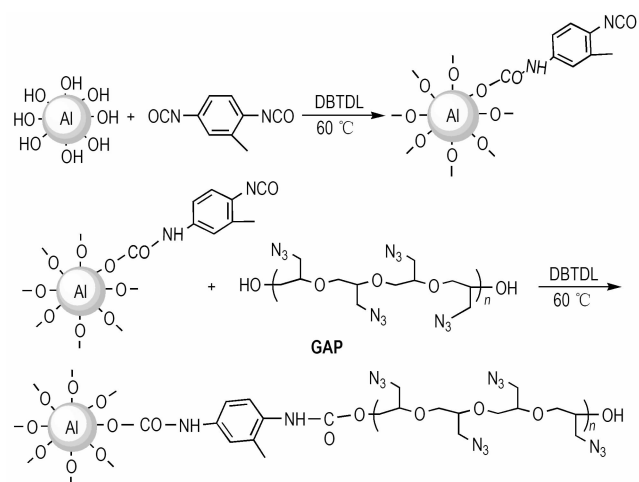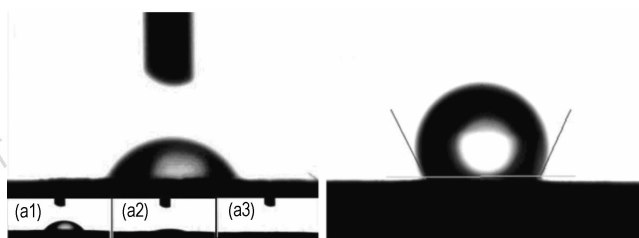

Fig. 1 Surface grafting GAP onto aluminum powders

The morphology was examined by scanning electron microscopy (APOLLO 300, CAMSCAN). The surface properties of aluminum powders were investigated by measuring static water drop contact angle with the sessile drop method (SL 200B). The aluminum powders were pressed into $\Phi10 \ mm \times 2 \ mm$ pellet. Water was dropped onto the surface of pellet and the contact angle was recorded from photograph. To test the effect of surface grafting of GAP on the protection of aluminum from being oxidized by water, stability test for aluminum powders was conducted in water at 70 ℃. The conversion of aluminum was calculated by $[Al]_{conv}/[Al]_{total}$, where $[Al]_{total}$ is the total active aluminum of the aluminum powders, $[Al]_{conv}$ is amount of consumed active aluminum, which is calculated based on $[Al]_{conv} = 27pV/RT$, herein, $p = 1.01 \times 10^5$ Pa, $T = 298$ K, V is the volume of released hydrogen from the reaction of aluminum and water as prolongation of time, which was measured by water drainage method.

3 Results and discussions

3.1 Surface properties

The surface property of the aluminum powders was studied by measuring static water contact angle on the surface of aluminum powders. The aluminum powders were pressed into $\Phi10 \ mm \times 2 \ mm$ pellet. Water was dropped onto the surface of pellet. It is clearly seen from Fig. 2a that water can easily permeate the surface of the fresh aluminum powders pellet. The static water contact angle on the fresh aluminum powders is in a range of 0° and 25.7°. After surface grafting with GAP molecules, as shown in Fig. 2b, water drop can steadily stay on the surface of the pellet, and the static water contact angle is 109.9°. It indicates that the surface property of aluminum powders can be significantly changed from hydrophilic to hydrophobic by a little grafting of GAP molecules due to the highly apolar azide groups of the GAP polymer chains. This change in surface property will lead to improvement of adhesion of aluminum powders by organic binders.
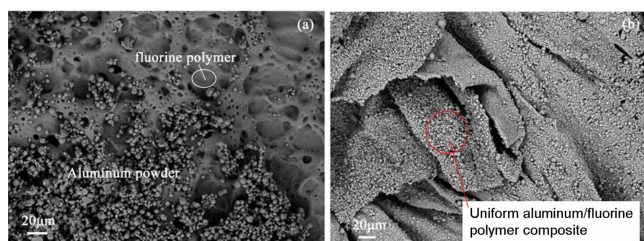

a. fresh aluminum surface   **b.** GAP-grafted aluminum surface
Fig. 2 Photoes of static water contact angle measurement on different surface

The effect of surface modification on the compatibility of aluminum powders with the organic bindersis showed by preparation of aluminum/fluorine polymer composite. The fluorine polymer is chosen because it is widely used as polymeric binders in aluminized explosives. But it difficultly adheres onto the aluminum powders, due to large polarity difference between aluminum powders and fluorine polymers. In this work, the aluminum powders are mixed in fluorine polymer solutions, then the mixture is dropped into water, and the Al/fluorine polymer products is obtained by filtering water and organic solvents. As can be seen from Fig. 3a, for the unmodified aluminum powders, it is hardly wetted and adhered by the fluorine binders. The SEM image clearly shows the aggregation of

the aluminum powders and floated on the polymer film. For the GAP-grafted aluminum powders, the aluminum paticles disperse in the fluorine binders and form uniform aluminum/fluorine polymer composite. SEM image shows that high density of modified aluminum powders are homogeneously distributed in the fluorine polymer matrix (Fig. 3b). The surface grafting of GAP not only effectively breaks up the aggregation of Al particles, but also improves the wetting characteristics at the phase interface with fluorine polymers.

a. fresh aluminum powders   **b.** GAP-grafted aluminum powders
Fig. 3 SEM images of aluminum/fluorine polymer composite with different aluminum powders

3.2 Stability in water

The results for stability test in water at 70 ℃ for the fresh aluminum powders, aluminum powders coated with 1.5% No. 70 wax, aluminum powders coated with 1.5% fluorine polymer and GAP-grafted aluminum powders are shown in Fig. 4. The following observations can be made.

(1) The fresh aluminum powders were quickly reacted: 39.8% of active aluminum was oxidized after 15 min and 51.8% of activated aluminum was oxidized after 30 min.

(2) The conversion trends of the two physical coated samples, the wax coated aluminum and fluorine polymer coated aluminum are similar with the fresh aluminum powders, indicating that physical coating can not effectively prevent the oxidation of aluminum in hot water.

(3) Only 1.4% of GAP-grafted aluminum powders was reacted after 60 minutes, showing that the GAP-grafted aluminum powders have better water oxidation-resistance ability.
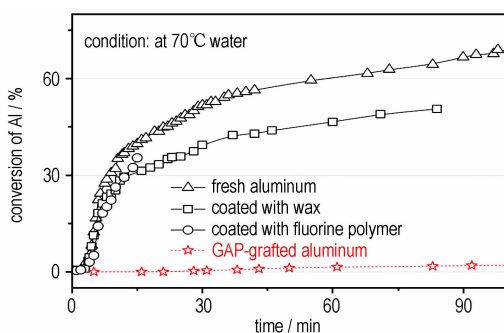

Fig. 4 Conversion of Al vs time for four kinds of aluminum powders by stability test in water at 70 ℃

4 Conclusion

(1) The surface of ultrafine aluminum powders is modified via grafting with GAP molecular.

(2) The static water contact angle is 0-25.7° for the

fresh aluminium powders and 109.9° for GAP-grafted aluminium powders.

(3) The GAP-grafted aluminum powders exhibit good compatibility with fluorine polymers, which will provide a beneficial route for formulation of aluminum powders and strengthen of aluminum/polymer composites.

(4) GAP-grafted aluminum powders have better resistance to water oxidation. Only 1.4% of GAP-grafted aluminum powders are reacted after 60 min in water at 70 ℃, providing a potential route to produce aluminized explosive formulations in water.

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表面接枝 GAP 改性超细铝粉的制备与性能

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摘　要： 用二异氰酸酯作桥，通过—OH 和—N＝C＝O 基团间的连串缩合反应，经过接枝含能端羟基叠氮缩水甘油醚（GAP），改性了超细（1～2 μm）铝粉表面。研究了接枝 GAP 铝粉的表面性质，与含氟粘结剂的相容性及 70 ℃水中稳定性。结果表明，接枝前后的铝粉表面静态水滴接触角分别为 0～25.7°和 109.9°，表面接枝后，铝粉表面性质从亲水改变为疏水。接枝 GAP 的铝粉与含氟粘结剂有更好的相容性。在 70 ℃水中 15 min 后，未经处理的铝粉有 39.8%的活性铝被氧化，而经过 GAP 接枝改性的铝粉在 70 ℃水中 60 min 后只有 1.4%的活性铝被氧化，显示接枝 GAP 的铝粉可有效保护铝粉在苛刻的热水条件下不被氧化。

关键词： 含能材料；超细铝粉；端羟基叠氮缩水甘油醚（GAP）；表面接枝