Effect of hydrogen storage alloy on combustion properties of ammonium perchlorate /glycidylazide polymer -based propellant

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Abstract. Hydrogen storage alloys can serve as good potential fuels for propellant design, by improving the energy and combustion properties. The influence of hydrogen storage alloy (A30) on the combustion properties of ammonium perchlorate/glycidylazide polymer (AP/GAP)-based propellant were studied. The results showed that A30 could increase the burning rate of propellants by 29.75% and 74.78%, compared with B30 and Al. The combustion model of AP/GAP-based propellant containing different fuel was built. Firstly, A30 reduced the high decomposition temperature and promote condensed phase reaction heat of AP. Secondly, A30 deduced the burning surface temperature. Thirdly, A30 might prove the explosive heat of propellant. Therefore, A30 could greatly improve combustion properties of AP/GAP-based propellant.

1. Introduction
Raising the energy stored in a material has been the main line of the development for solid propellant technology. High formation enthalpy, low gas molecular weight and high combustion heat release of the propellant components all contribute to improvement in the propellants energy. Some important areas include the developments and applications of new energetic binders, high-energy oxidants and energetic plasticizers [1-3]. Introducing a certain amount of H into metal fuel is a feasible way to raising its energy performance. H₂ has a high combustion heat value up to 142900 kJ/kg [4]. Besides, H₂O generated from the combustion of H₂ has the smallest molecular weight among all the oxides. Therefore, propellant energy performance could be improved by using a combustion agent containing H in place of conventional metal fuel. In recent years, AlH₃[5, 6] has been received extensive attention because it can significantly improve specific impulse of the propellant, and yet it has not been applied extensively due to its poor stability and compatibility. Hydrogen storage alloy, by contrast, is a potential combustion agent because of its controlled alloy structure and adjusted performances in a wide range. A30 is a new kind of hydrogen storage alloy whose structure is MgNiB-Al and contains 70% Al and 0.98% H, wherein H exists as MgH₂ form and releases from it at 372.24 °C (DSC data, 0.1 MPa) and has a good stability [7, 8]. A30 (31525 kJ/kg) has a higher combustion heat than Al (25500 kJ/kg), so it can improve the energy level of the propellant and has a good application prospect when used instead of Al. In our work, A30 is applied into AP/GAP-based propellant and combustion
properties are investigated, which will lay the foundation for further applications of hydrogen storage
alloys in AP/GAP-based propellants.

2. Experiments

2.1. Materials and specimen
Al(13 μm), B30 (B30 has the same structure with A30 but for the hydrogen storing characteristic, 16
μm) and A30 (16 μm) was used as fuels to prepare respectively AP/GAP-based propellants coded for
GA0, GB30 and GA30 separately. Propellant formulation was as follows: (GAP + N100): 14%, AP:
63%, Fuel:17%, others:6%.

2.2. Equipment and experimentations

2.2.1. Burning rate. Strand burner method was adopted to test propellant burning rate at 20°C, N2
atmosphere and 3 MPa, 5 MPa, 7 MPa, 9 MPa pressure. The burning rate at each pressure was the
average value of 5 duplicate results. And pressure exponents are got according to Vieille burning rate
equation \( u = u_1 p^n \) by line regression.

2.2.2. Condensed phase reaction performance. Condensed phase reaction performance was
characterized by thermo gravimetry (TG)-differential scanning calorimetry (DSC) analyzer of TG-
DSC1 type produced by METTLER company at the condition of 2.0 mg sample weight, N2
atmosphere, 40 ml/min gas flow rate, Al2O3 crucible, 10 °C/min heating rate and 0.1 MPa pressure.

2.2.3. Burning surface morphology. Steady state quenched surface sample was obtained employing
thermal contact conductance method [5] in closed system under N2 atmosphere, 5 MPa pressure and
22°C ignition temperature. And then, quenched surface morphology is characterized by JSM-5800
type scanning electron microscope (SEM) produced by Japan.

3. Results and discussions

3.1. Burning rate
Burning rates of AP/GAP-based propellants with different fuel at 3~9 MPa and the corresponding
pressure exponents \( (n) \) were all listed in Table 1. As could be seen in table 1, GA30 had a lower
pressure exponent and the highest burning rates among three kinds of propellants. Burning rate of
GA30 was increased by 29.75% and 74.78% respectively compared to GB30 and GA0 at 5 MPa. In
order to find the reasons, the combustion models of AP/GAP-based propellants were studied as
following.

Table 1. Burning rates and pressure exponents for three kinds of propellants.

| Samples | Burning rates/(mm/s) | 3 MPa | 5 MPa | 7 MPa | 9 MPa | n  |
|---------|---------------------|-------|-------|-------|-------|----|
| GA0     |                     | 6.43(0.23)* | 7.81(0.07) | 8.38(0.06) | 8.94(0.10) | 0.2901 |
| GB30    |                     | 9.86(0.28) | 10.34(0.14) | 10.52(0.11) | 11.56(0.32) | 0.1330 |
| GA30    |                     | 12.90(0.02) | 13.65(0.19) | 14.91(0.13) | 15.73(0.27) | 0.1869 |

\*\*\* value in parentheses represents variance of the 5 sample results.

3.2. TG/DSC
Condensed phase reaction performance of propellant at steady state could be reflected by
decomposition performance, so TG/DSC is a reliable mean for researching the effects of A30 on
AP/GAP propellant condensed phase reactions. TG and DTG curves of 30, GB30 and GA0 were
shown in figure 1 and DSC data was listed in table 2.
As is seen from figure 1, the TG curve of GA0 was divided into 4 zones assigned into volatilization of the plasticizer, decomposition of GAP, decomposition of AP at lower and higher temperature respectively. Other from these, there was one another decomposition area belonging to the further decomposition of AP only in GB30 and GA30. So, B30 and A30 had little effect on decomposition of GAP. But, the effect of B30 and A30 on AP was obvious, for example, low-temperature decomposition peak (TL) of AP was the main exothermic peak for GA0, but higher-temperature decomposition peak (TH) of AP was the main exothermic peak for GB30 and GA30. Possible reasons for the additional decomposition process of AP in GB30 and GA30 was as follows: Compared to GA0, GB30 and GA30 produced a large amount of gas in the fourth area at a lower temperature as results of their intense reaction activities. The generated gases covered over AP surface to affect its decomposition performance, and when reaction active centers of AP are completely covered, low-temperature decomposition of AP terminated. At this situation, there was a part of undecomposed AP. This remaining AP would go on decomposing when the covered gases left again at a higher temperature and formed the fifth decomposition zone. If the interference is right, there will be the following conclusions: the more violent reactions of AP higher-temperature decomposition are, the more generated gases are, the stop temperature of AP higher-temperature decomposition is, and the higher of step AP decomposition temperature is. And this might be proved by GB30’s lower fifth decomposition peak temperature compared to GA30.

It was shown from table 2 that B30 and A30 do not substantially affect GAP thermal decomposition heat possibly because of the low activities between fuel and GAP and the corresponding generated oxidizing gases, but could largely increase AP thermal decomposition heat generation, and total heat generations with respect to GA0 have the increase of 2.07% and 2.57% respectively, because of the high combustion heats of B30 and A30, which increase the condensed phase reaction heat generations of GB30 and GA30 at the same reaction rates between fuel and oxides.

**Figure 1.** TG and DTG curves of GA30, GB30 and GA0.

**Table 2.** DSC data of GA30, GB30 and GA0.

| Propellants | Heat generations/ (J/g) | Total heat generations/ (J/g) |
|-------------|-------------------------|------------------------------|
|             | Secondary zone *        | Tertiary and fourth zone     | Fifth zone                  |
| GA0         | 157.45                  | 277.96                       | -                           | 435.41                      |
| GB30        | 165.39                  | 1140.62                      | 30.05                       | 1336.06                     |
| GA30        | 158.39                  | 1369.25                      | 28.63                       | 1556.27                     |

*Note: Heat generation of the secondary area is only the heat generation of GAP bind decomposition*
3.3. Quenched surface morphology and residual elements
Steady state burning surfaces of GA30, GB30 and GA0 propellants at a certain pressure could be preserved by the quick flameout method shown in figure 2.

![Figure 2](image)

**Figure 2.** Quenched surface SEM images (100 times) and the corresponding EDS images of 3 propellants at 5 MPa.

GA0 quenched surface was flat and had spherical particles connecting with each other by coral-like materials. And with further amplified, it can be seen from the images (figure 2) that the spherical particles were surrounded with much smaller ones. EDS analysis showed that spherical particles are the melt and partially oxidized Al particles, and the coral-like materials are residual carbons generated from the decomposition of binder and other organic components. Similar spherical particles and coral-like materials which were alloy particles that were much larger and widely oxidized are also appear on GB30 quenched surface. At the center and upper left side of GB30 SEM image (figure 2) there were some irregular smooth large particles which were also alloy particles exist. These particles were at the transition state between small and large particles and were preserved due to rapid flameout. GA30 had the similar quenched surface with GB30, but for the very irregular surface and the less oxidized spherical particles rising above the surface. At the top left of GA30 SEM image (figure 2), there was an alloy group in maximum size, which had already been melted and got ready to leave the burning surface but was preserved by sudden flameout. Apart from this one, the sizes of other particles are all smaller than that of GB30 alloy particles. The cause of phenomena may be with the combustion process of fuel in propellant. For example, combustion of Al in composite propellants has to go through the following processes [9]: melted, accumulated, ignited and leave from burning surface. It
can be known from Al ignition model [9] shown in figure 3(a) that main heats supporting the above processes of Al were supplied by diffusion flames generated from combustion of heterogeneous AP and premixed flame generated from combustion of binder. Al started to melt while the temperature is higher than its melting point (660°C), and then the neighboring Al accumulated together until ignitions happen. Diameter of Al particles in GA0 quenched surface is up to 0.3~0.4 mm which is bigger than that of raw materials, also proving the occurrence of the above processes. Furthermore, condensed phase reaction heat and gas phase reaction heat passing onto the burning surface with conduction and feedback ways would also accelerate occurrence of the whole above processes. Ignition model of B30 was established based on Al ignition model shown as figure 3(b). These models of B30 and Al were similar but for the following differences. Firstly, Mg/Al alloy in B30 made it easy to be ignited which makes GB30’s burning rate higher than GA0. Secondly, B30 could form bigger alloy particles easily at a fixed temperature because of its lower melt point (652°C, DSC data). A30 ignition model was established based on B30 ignition model shown as figure 3(c). There were some new features compared with B30 ignition model. Firstly, A30 had a hydrogen release process before melted and accumulated. Secondly, A30 melting point 657°C (DSC data) after hydrogen release was higher than B30 which is advantageous in forming little size alloy particles. Thirdly, more heat would be generated from H₂ combustion which could reduce ignition time. Finally, the size of A30 is smaller and specific surface area of A30 was bigger after hydrogen release and alloy powdered process which will be advantageous in shorting ignition time and reducing alloy sizes.

In addition, the huge Al or alloy particles on burning surface of GA30, GB30 and GA0 were also affected by the combustion performances of GAP binder (figure 4). Cured GAP binder has a bubble zone according to its combustion model [10] shown in figure 4. GAP decomposed and generated initial gas and liquid products, then some evaporating liquid products together with gas products to form one after another bubbles in which gas-gas reactions occur. Therefore, coexistence of condensed phase and gas phase was the most important feature of this zone. And then gases were sharply produced at the burning surface of GAP binder. Further thermal decomposition and oxidation-reduction reactions were proceeding around nearer burning surface to produce huge heat. Burning surface temperature of GAP binder was about 427~527°C, lower than any burning surface temperature of GA30, GB30 and GA0 (table 3). Therefore, it can be deduced that combustion heat of GAP is
largely absorbed by burning surface of the GA30, GB30 and GA0 which is positive to form huge Al or alloy particles.

Table 3. Explosion heats and burning surface temperatures of GA30, GB30 and GA0.

| Propellants | Explosion heats/(kJ/kg) | Burning surface temperatures/℃ |
|-------------|------------------------|-------------------------------|
| GA0         | 6135                   | 738.53                        |
| GB30        | 6592                   | 774.52                        |
| GA30        | 6604                   | 668.67                        |

So, the combustion model of propellant was different, when the fuel was A30, B30, Al. At the same, the fuel might affect the energy level of propellant. Seen from table 3, the explosion heats of GA30 was largest in the three kinds of propellant caused by easier ignition performance, higher combustion heat and higher combustion efficiency of A30.

4. Conclusions
It is found that alloy compositions and hydrogen storage/release properties of hydrogen storage alloy were all favored the combustion performances of AP/GAP-based propellant. Alloy compositions favored the improvement of its combustion heat and further the level of condensed phase reaction heat and explosion heat of the propellant. Catalysis of hydrogen storage alloy to AP was reflected on its influences to decomposition of AP, making high decomposition temperature of AP decreased and decomposition reactions of AP more violently. Ignition and energy performances of the propellant were improved due to hydrogen storage/release and H₂ combustion properties of A30. Ignition performance can be further improved owing to powder feature of A30, which also promotes both condensed phase and gas phase reaction efficiencies of the propellant. Easier ignition performance, higher combustion heat and higher combustion efficiency of hydrogen storage alloy were the main reasons to make AP/GAP-based propellant have much marked improvements. Besides, the released H₂ which has acceleration effect on the leave of the components at burning surface is one another reason to the improvements of combustion performance of the propellant.

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