INTRODUCTION

It is known that superfine aluminum powders (SFAP) can successfully replace the micron-sized aluminum powders (10–100 μm) in propellants. Such substitution leads to an increase in the combustion efficiency of aluminum and also leads to decreased agglomeration of the combustion products and reduction of two-phase losses [1, 2]. The decrease in the size of aluminum particles and increase in the reaction’s surface area, considerably increase the combustion rate of the propellant composition [1]. SFAP obtained by the electrical explosion of wires (EEW) has been studied in detail [3–9], and interest in such SFAP continues to rise [10]. The formation of particles under conditions of electrical explosion (power density $>10^{13}$ W/cm², time of process 1–10 μs) can lead to the stabilization of metastable energy-saturated structures, which relax at relatively low temperatures and increase the reactivity of SFAP [11]. An increase in the dispersiveness of SFAP leads to an increase in their reactivity. But the basic problem of using SFAP is the relatively low content of metallic aluminum (93–97 mass %) [5, 6] simultaneously with the high reactivity of SFAP. Another problem of using superfine powders as additives to propellants is the original agglomeration of SFAP when produced by EEW. The original agglomeration of SFAP is connected with the reactivity of the particles’ surfaces, and the necessity for particles to concentrate and collect in the gas-phase. The agglomerates of SFAP in the porous structures consist of superfine particles in the state of the primary stage of sintering. Between the particles (d <0.05 μm) are contact zones which slightly change the shape of the particles. The presence of agglomerates of particles leads to heterogeneity of the mixtures and to coalescence of agglomerates in the heat penetration zone during combustion. In this case large drops are formed, so the advantages of using SFAP are lost.

It has been experimentally established that additives to the Ar gas used in EEW, such as chemically active gases (O₂ and N₂), lead to the products from EEW being more dispersed [4]. Reduction of particle size in this case is because of a decrease in agglomeration and sintering during EEW. The presence of high-melting point non-metallic compounds (AlN, Al₂O₃) on Al particles also reduces agglomeration during the heating of SFAP during combustion, analogous to when aluminum particles are encapsulated by high-melting point metals (Cu, Ni, Fe) [12]. If the stabilization of SFAP is because of the formation of an oxide film, it leads to the loss of 3 to 5 mass % of aluminum and to a decrease in the combustion enthalpy of the powder. In other words, to stabilize SFAP it is necessary to cover them by a film obstructing future oxidation. If such a film is Al₂O₃ the content of metallic aluminum is just 93 to 97 mass %. Additionally, the Al₂O₃ is the substance containing aluminum in its highest degree of oxidation (Al³⁺), which is inert during combustion. By adding nitrogen to argon during EEW, the dispersity of the powders obtained increases, and a coating of AlN can be produced in the electrical explosion [4].
tion in air (this stage is necessary to stabilize powders), however, AlN is oxidized and hydrolyzed; therefore the protecting film in this case is $\text{Al}_2\text{O}_3$ with some $\text{Al(OH)}_3$. Thus, qualitative improvements in the reactivity and characteristics of SFAP are needed.

As an alternative to a protective film of oxide, aluminum diboride ($\text{AlB}_2$) as a coating is offered in this present work. Such a coating of particles forms during EEW [13] in contrast to the oxide coating, which forms after EEW by passivation. In this case, unlike the inert aluminum oxide coating, the combustion of aluminum diboride coating is exothermic by 41337 kJ/kg of heat: the passivation layer is thus a material with a high enthalpy.

**EXPERIMENT AND DISCUSSION**

Boride-encapsulated particles of SFAP were obtained by EEW of aluminum wires with a boron-containing coating. From the EPMA (Electron Probe Micro Analysis) data plotted in Fig. 1, it was shown that the composition of the coating is close to $\text{AlB}_2$. X-ray diffraction (XRD) analysis of SFAP only indicates the presence of an aluminum phase; thus $\text{AlB}_2$ is not detected, clearly, because of the amorphous characteristics of the coating. A SEM-photograph of these SFAP is given in Fig. 2, which reveals that the particle sizes are not uniform. In fact, most particles have a diameter less than 100 nm. Producing EEW-powders with a narrower particle size distribution is possible by increasing the energy liberated in the wire and by using chemically active gases [4] or reagents.

**TABLE 1**

Characteristics of SFAP Obtained by EEW Method

<table>
<thead>
<tr>
<th>No</th>
<th>SFAP (cover film)</th>
<th>Gas-media</th>
<th>$e/e_{\text{Al}}^\text{e}$, arb. unit</th>
<th>$S_\text{(BET)}, \text{m}^2\text{g}$</th>
<th>$[\text{Al}]^\text{III}$, mass %</th>
<th>$[\text{Al}_2\text{O}_3]^\text{d}$, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Al(AlB}_2\text{)}$</td>
<td>Ar</td>
<td>1.38</td>
<td>17.0</td>
<td>78.0 + 18.0% $\text{[AlB}_2\text{]}$</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Al(Al}_2\text{O}_3\text{)}$</td>
<td>Ar</td>
<td>1.45</td>
<td>9.3</td>
<td>88.5</td>
<td>5.5</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Al(Al}_2\text{O}_3\text{)}$</td>
<td>Ar + N$_2$</td>
<td>1.64</td>
<td>16.0</td>
<td>89.0</td>
<td>5.0</td>
</tr>
<tr>
<td>4*</td>
<td>$\text{Al(Al}_2\text{O}_3\text{)}$</td>
<td>Ar</td>
<td>2.15*</td>
<td>12.1</td>
<td>94.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>

* Alex (Argonide Corp.) [15].

* $e/e_{\text{Al}}^\text{e}$-specific electrical energy liberated in the wire [4] (ratio of electrical energy liberated in the aluminum wire to the energy of sublimation of $\text{Al} e_{\text{Al}}^\text{e} = 12208$ kJ/kg).

* Calculated theoretically by correlation equation [8].

* SFAP also includes some absorbed gases (not calculated in this Table).
The characteristics of SFAP with aluminum diboride coatings are given in Table 1, together with those of other types of SFAP for comparison.

During EEW the initial products of electrical explosion \( (T \sim 10^4 \text{ K}) \) are cooled below the upper temperature boundary of the chemical reactions \( (T \sim 5 \times 10^3 \text{ K}) \). At such temperatures, because of the presence of reagents, the formation of refractory compounds occurs. This decreases the original agglomeration of particles and their sintering. The presence of boron (sample No. 1) or the addition of nitrogen to argon (sample No. 3) during the electrical explosion actually leads to an increase by almost a factor of 2 in the specific surface area \( (S_s) \) of SFAP, in comparison with the SFAP obtained in argon (sample No. 2 in Table 1). In this case the specific electrical energy liberated in the wire \( (e/e_s) \) increases insignificantly for samples No. 1 to 3, that is, the power expenditure for metal dispersion (formation of 1 m\(^2\) of surface) because of the presence of additives (samples No. 1 and No. 3) is reduced about a factor of 2 (see Table 1). The analysis of the reactivity of SFAP was carried out through the previously proposed parameters [14], derived from differential thermal analysis of SFAP samples at standard conditions. The reactivity of SFAP, which characterizes their behavior in oxidized media was determined from four parameters:

- The temperature for the onset of intensive oxidation \( (t_{\text{on}}, \degree\text{C}) \).
- The maximum rate of oxidation \( (v_{\text{ox}}, \text{mg/min}) \).
- The degree of conversion (degree of oxidation) of Al in a certain range of temperatures \( (\alpha, \%) \).
- The ratio of the oxidation thermal effect (from the area of the peak under a DTA-curve) to the corresponding value of the mass increase (from a TGA-curve) of the analyzed sample \( (S/\Delta m, \text{arb. unit}) \).

The standard mass of SFAP samples under investigation was \( \sim 5 \times 10^{-5} \text{ kg} \); the rate of heating was \( \sim 10^\circ\text{C/min} \) in the DTA/TGA-analyzer. Parameters for the reactivity of SFAP and of SFAP “Alex” (Argonide Corp.) are compared in Table 2. According to Table 2, coating the particles with aluminum diboride increases the thermal stability of SFAP. Thus, the temperature for the onset of intensive oxidation rises by 30 to 40\( ^\circ\text{C} \) in comparison with SFAP with a coating of oxide-hydroxide. The degree of oxidation of sample No. 1 (with the AlB\(_2\)-coating) during heating to 660\( ^\circ\text{C} \) is lower by \( \sim 6 \) to 16\% than with sample Nos. 2 to 4, which begin to be oxidized at a lower temperature. During the heating to 1000\( ^\circ\text{C} \), the majority (70–78.5\%) of the SFAP is oxidized: there remained only either drops, which are formed during the coalescence and sintering of SFAP particles, or particles of micron sizes. Less than half (45.0\%) of sample No. 4 is oxidized during heating to 1000\( ^\circ\text{C} \). Oxidation of sample No. 4 at a temperature above 1000\( ^\circ\text{C} \) occurs analogously with the oxidation of micron-sized powders [5, 14]. The values of the maximum rate of oxidation \( (V_{\text{ox}}) \) for sample Nos. 1, 3, and 4 are not much different, but the maximum value of \( V_{\text{ox}} \) is that for sample No. 2 with the largest particles (see Table 1). The higher rate of oxidation of sample No. 2 can be attributed to relaxation processes (defects annihilation, amorphous phases crystallization, and so forth). An inverse dependence between the maximum rate of oxidation \( (V_{\text{ox}}) \) and the experimentally determined thermal effect \( (S/\Delta m) \) is also observed. It is

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### Table 2

<table>
<thead>
<tr>
<th>No</th>
<th>( t_{\text{on}}, ^\circ\text{C} )</th>
<th>( \alpha_1 (&gt;660\degree\text{C}), % )</th>
<th>( \alpha_2 (&gt;1000 \degree\text{C}), % )</th>
<th>( v_{\text{ox}}, \text{mg/min, (t, }^\circ\text{C}) )</th>
<th>( S/\Delta m, \text{arb. unit} )</th>
<th>( \text{Calculated } \Delta H_{298^\circ}, \text{kJ/kg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>580</td>
<td>34.0</td>
<td>77.8</td>
<td>3.2 (580–600)</td>
<td>6.3</td>
<td>31635</td>
</tr>
<tr>
<td>2</td>
<td>540</td>
<td>40.0</td>
<td>70.0</td>
<td>5.6 (545–570)</td>
<td>5.6</td>
<td>27451</td>
</tr>
<tr>
<td>3</td>
<td>540</td>
<td>49.7</td>
<td>78.5</td>
<td>3.0 (550–605)</td>
<td>8.7</td>
<td>27607</td>
</tr>
<tr>
<td>4*</td>
<td>550</td>
<td>39.4</td>
<td>45.0</td>
<td>3.0 (541–555)</td>
<td>—</td>
<td>29406</td>
</tr>
</tbody>
</table>

*Alex (Argonide Corp.) [15].
possible to explain this dependence as because of an increase in the heat losses at higher rates of oxidation (see Table 2). Thus, the SFAP obtained with the AlB$_2$ coating has a higher reactivity than the SFAP obtained by EEW under the offered parameters [14]. The calculated combustion enthalpies of all the samples being studied show that replacing the oxide-hydroxide film on particles with a film of AlB$_2$ during combustion gives an additional (2.2–4.1) $\times 10^3$ kJ/kg of heat. Moreover, the presence of boron as AlB$_2$ in a composition can promote the gasification of the metal and increase the combustion temperature [16].

CONCLUSIONS

Aluminum diboride coating, as applied to SFAP particles in the process of electrical explosion of aluminum wires, leads to an increase in the dispersiveness by $\sim 2$ times because of lower agglomeration. The properties of SFAP particles with the diboride coating are changed: their thermal stability (on 30–40°C) is higher than SFAP obtained in an Ar medium or in a medium of Ar with N$_2$. The significant part (more than 40 mass %) of SFAP, passivated with AlB$_2$, is oxidized in the range of temperatures from 660°C to 1000°C. SFAP with a covering of AlB$_2$ gives an additional (2.2–4.1) $\times 10^3$ kJ/kg of combustion enthalpy than other SFAP obtained by EEW. In the future it would be interesting to check the reactivity of SFAP coated with AlB$_2$ in AP/HTPB/Al propellants.

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REFERENCES