Aluminum powders: aging effects on metal content and thermogravimetry reactivity

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Abstract
Nano-sized Al (nAl) features high reactivity implying possible issues related to its aging during storage. In this work, the aging behavior of micron-sized Al and nAl is investigated considering different relative humidity (RH) conditions (10% and 80%) at the temperature of 333 K. The marked aging sensitivity of nAl (100 nm) is testified by an almost full metal content (C_m) loss in nearly 30 hours (RH = 80%). Under the same condition, in 14 days of aging, the C_m of micron-sized aluminum (30 μm) decreases from (99.1 ± 0.2)% to (86.8 ± 0.9%).

Keywords: nano-sized aluminum, micron-sized aluminum, aging, metal content, thermogravimetry reactivity

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>D_mean</td>
<td>surface-based mean particle diameter [nm]</td>
</tr>
<tr>
<td>T_ox</td>
<td>i-th intense oxidation end temperature [K]</td>
</tr>
<tr>
<td>T_oox</td>
<td>i-th intense oxidation onset temperature [K]</td>
</tr>
<tr>
<td>a_Alol</td>
<td>Al → Al₂O₃ conversion factor, Δm(T)/C_A*0.89 [%]</td>
</tr>
<tr>
<td>a_Alohy</td>
<td>Al → Al(OH)₃ conversion factor, Δm(T)/C_A*1.889 [%]</td>
</tr>
<tr>
<td>Δm</td>
<td>mass change due to desorption/dehydration [%]</td>
</tr>
<tr>
<td>Δm_1</td>
<td>mass change in the first oxidation step [%]</td>
</tr>
<tr>
<td>Δm_93K</td>
<td>mass change at 933 K [%]</td>
</tr>
<tr>
<td>Δm_1223K</td>
<td>mass change at 1223 K [%]</td>
</tr>
</tbody>
</table>

1. Introduction
Aluminum is a high density energetic material widely used in solid propellants and fuels for rocket propulsion. Currently, commercial solid propellants are based on air-passivated micron-sized aluminum (μAl) with size in the range 50–15 μm. These powders are characterized by metal contents (C_m) typically higher than 95 wt%, and specific surface area (SSA4) lower than 1 m² g⁻¹. Nano-sized Al (nAl) features increased reactivity over the conventional μAl. In general, air-passivated nAl exhibits SS4 ≥ 10 m² g⁻¹, and C_m < 90 wt%. While attractive in terms of the enhanced performance in a combustion environment, nAl high reactivity may yield issues related to aging under storage. Few open literature studies deal with the aging process of Al powders, while aging effects (under non-fully controlled/reported conditions) are observed in different publications.

This paper investigates the accelerated aging behavior of aluminum powders with various particle sizes. Tested powders range from conventional μAl to nAl. The collected data show the aging effects on powder energetic content (C_m) and reactivity (evaluated by thermogravimetry, during slow heating rate oxidation).

2. Materials and experimental methods
2.1 Tested powders
Tested powders are commercially available, uncoated and passivated by air. Micron-sized powders (μAl-30, and μAl-7.5) are produced by AMG Alpoco (UK). The nAl powder (nAl-100) is produced by APT-Advanced Powder Technology LLC (Russia).

2.2 Powder characterization
Tested powders were characterized in terms of particle size distribution by Malvern Mastersizer 2000, using both dry and liquid dispersion units (for micron- and nano-sized...
materials, respectively). The specific surface area was determined by N\textsubscript{2} adsorption/desorption isotherms and the BET equation\textsuperscript{13}. The \(C_a\) was evaluated by a volumetric method based on the Al+H\textsubscript{2}O reaction\textsuperscript{11,12,13}. Thermogravimetry (TG) analyses were performed in air, with heating rate of 10 K min\textsuperscript{-1}. Powder reactivity was determined exploiting the parameters suggested by Ilyin et al\textsuperscript{13}.

### 2.3 Aging conditions

The aging of the powders was studied under a temperature of 333 K, to accelerate the corrosion process. Two different conditions of RH were considered to highlight the effects of the H\textsubscript{2}O vapor concentration. In the dry environment D1 condition, RH < 10\% (dry air + SiO\textsubscript{2}), while in the humid environment H1 condition RH = (80.2 ± 0.4)\% (saturated H\textsubscript{2}O + KCl solution). Accelerated aging conditions were produced in sealed glass containers with internal volume of 0.5 dm\textsuperscript{3}. These vessels were prepared and stored at \(T = 333\) K for 24–48 hours, before the start of the experiments. Small amounts of powder (0.3–0.4 g) were inserted in glass weighing bottles with diameter of 30 mm. The (opened) weighing bottles were placed in small plastic jars and were then inserted in pre-prepared, sealed glass vessels containing the test environment. The reduced amount of powder granted a uniform exposure of the sample to the aging environment without any mixing.

### 3. Experimental results and discussion

Experimental results are hereby presented for the initial powder characterization and for the aging study. Thermal analysis data and \(C_a\) results are presented as average of at least two and four different runs respectively. In both cases, intervals of confidence are reported in terms of standard deviation.

#### 3.1 Initial characterization

The tested air-passivated powders are listed in the Table 1. Micron-sized powders show \(D_{50}\) values in agreement with the nominal size. The μAl-7.5 features \(D_{50} = 4150\) nm, due to a bimodal distribution with a small powder fraction (< 3.0 vol.\%) of sub-micrometric size (400–1000 nm). The nAl-100 SSA-based particle diameter\textsuperscript{13} (\(a\)) shows a general agreement with the \(D_{50}\) from laser granulometry. X-ray diffraction analyses performed on the fresh powders revealed metallic Al as the unique crystalline phase in the materials. Scanning and transmission electron microscopies of the tested powders are reported elsewhere\textsuperscript{13}. TG traces for the non-isothermal oxidation of μAl-30, μAl-7.5 and nAl-100 are reported in the Figure 1. The reactivity parameters for the TG analyses are presented in the Table 2. The powder first oxidation onset is below the Al melting point (933 K), and is related to the amorphous to α-Al\textsubscript{2}O\textsubscript{3} phase transition\textsuperscript{14}. The \(T_{\text{max},1}\) shows no clear correlation with the powder size, as evidenced by the intense oxidation onset temperature for the nAl-100 with respect to the μAl-7.5. The finer micron-sized powder features a faint and slow oxidation process, in turn yielding an apparent onset reduction when applying the tangent method (see Figure 1(b)). The increased SSA of nAl-100 yields an increased reactivity over the μAl-counterparts, as testified by the \(\Delta m_{\text{SSA}}\), \(\alpha_{\text{A}2\text{O}}/\gamma_{\text{A}2\text{O}}\) (933 K) and \(\alpha_{\text{A}2\text{O}}/\gamma_{\text{A}2\text{O}}\) (1223 K) values. For both the micron- and the nano-sized particles, the metal core melting does not affect the powder reactivity under the tested TG conditions.

#### 3.2 Aging effects

##### 3.2.1 Dry environment (D1)

Tests performed under RH < 10\% show a similar trend of the relevant parameters between μAl and nAl specimens (see Figure 2). The powder mass is nearly unchanged during a period of 14 days, independently from the powder dispersity. The relatively low H\textsubscript{2}O content in the aging environment limits the corrosion of the Al\textsubscript{2}O\textsubscript{3} shell (i.e., its transformation into hydrated species as Al(OH)\textsubscript{3}). Over the 14 days aging period, the \(C_a\) of μAl-30 shows no decrease. Similarly, the active metal content of μAl-7.5 shows values of (04.8 ± 0.4)\% at 7 days and (04.2 ± 0.6)\% at 14 days, being substantially unchanged. Active metal content of nAl-100 after 14 days of storage at RH < 10\% is (85.6 ± 0.3)\%. TG analyses show that after dry environment storage, nAl-100 mass loss due to the adsorbed gas desorption is (−0.9 ± 0.1)\%, while \(T_{\text{max},1} = (85.75 ± 0.1)\) K and the conversion factor from Al → Al\textsubscript{2}O\textsubscript{3} at 933 K and 1223 K are (38.7 ± 0.2)\% and (84.8 ± 0.6)\% respectively.

##### 3.2.2 Humid environment (H1)

For the H1 tests, the Al→Al(OH)\textsubscript{3} conversion factor \(\alpha_{\text{A}2\text{O}→\gamma_{\text{A}2\text{O}}} (t) = \Delta m(t)/(C_a = 1.889)\) is defined as a function of the aging time (\(t\)). The \(C_a\) (\(t\)) and the \(\alpha_{\text{A}2\text{O}→\gamma_{\text{A}2\text{O}}} (t)\) are shown in Figure 3 for μAl-30, μAl-7.5 and nAl-100. Note that the \(\alpha_{\text{A}2\text{O}→\gamma_{\text{A}2\text{O}}} (t)\) reflects the mass increase behavior of the tested powders. The powder SSA shows an influence on the powder aging, as shown in Figure 3.

Micron-sized powders exhibit an initial decrease of the \(C_a\) (\(t\)). This is then followed by a stabilization of the metal content in time. The μAl-30 shows a \(C_a\) change from

### Table 1

<table>
<thead>
<tr>
<th>Id.</th>
<th>Nominal size [nm]</th>
<th>SSA [m\textsuperscript{2} g\textsuperscript{-1}]</th>
<th>(a) [nm]</th>
<th>(D_{50}) [nm]</th>
<th>(C_a) [wt%]</th>
</tr>
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<tr>
<td>μAl-30</td>
<td>30000</td>
<td>&lt;0.1</td>
<td>&gt;22000</td>
<td>28800</td>
<td>99.1 ± 0.2</td>
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<tr>
<td>μAl-7.5</td>
<td>7500</td>
<td>&lt;0.1</td>
<td>&gt;22000</td>
<td>4150</td>
<td>95.3 ± 0.2</td>
</tr>
<tr>
<td>nAl-100</td>
<td>100</td>
<td>12.6 ± 0.1</td>
<td>176</td>
<td>133</td>
<td>85.7 ± 0.6</td>
</tr>
</tbody>
</table>
Figure 1  TG traces (air, 10 K min⁻¹, 0.1 MPa) of fresh (a) µAl-30, (b) µAl-7.5, and (c) nAl-100.

Table 2  Fresh Al powder reactivity parameters (TG, 10 K min⁻¹, air, 0.1 MPa).

<table>
<thead>
<tr>
<th></th>
<th>µAl-30</th>
<th>µAl-7.5</th>
<th>nAl-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δm [%]</td>
<td>0.2 ± 0.1</td>
<td>0.6 ± 0.3</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>T (Δm%) [K]</td>
<td>782.7 ± 2.1</td>
<td>741.2 ± 0.7</td>
<td>663.4 ± 1.9</td>
</tr>
<tr>
<td>T_melt [K]</td>
<td>865.0 ± 0.3</td>
<td>842.5 ± 0.5</td>
<td>856.1 ± 0.2</td>
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<tr>
<td>Δm_1 [%]</td>
<td>0.5 ± 0.1</td>
<td>1.8 ± 0.5</td>
<td>28.2 ± 0.4</td>
</tr>
<tr>
<td>T_melt [K]</td>
<td>915.3 ± 0.6</td>
<td>905.2 ± 0.4</td>
<td>898.4 ± 0.5</td>
</tr>
<tr>
<td>Δm_written [%]</td>
<td>0.5 ± 0.2</td>
<td>1.8 ± 0.5</td>
<td>29.5 ± 0.4</td>
</tr>
<tr>
<td>α_Ai-AsiO3 (933 K) [%]</td>
<td>0.6 ± 0.1</td>
<td>2.2 ± 0.6</td>
<td>38.7 ± 0.6</td>
</tr>
<tr>
<td>T_melt [K]</td>
<td>1224.2 ± 0.4</td>
<td>1203.3 ± 0.4</td>
<td>1014.9 ± 0.5</td>
</tr>
<tr>
<td>Δm_written [%]</td>
<td>NA.</td>
<td>NA.</td>
<td>NA.</td>
</tr>
<tr>
<td>α_Ai-AsiO3 (1223 K) [%]</td>
<td>2.5 ± 0.2</td>
<td>11.6 ± 0.5</td>
<td>65.6 ± 0.8</td>
</tr>
</tbody>
</table>

(98.1 ± 0.2)% to (86.8 ± 0.9)%, with a α_Ai-AsiO3 (14 days) = (4.7 ± 0.2)%. The µAl-7.5 shows a similar behavior, with C_Ai (7 days) = (38.1 ± 0.8)%. This value is further decreased to (55.8 ± 0.6)% for t = 14 days. The α_Ai-AsiO3 (14 days) is (21.3 ± 1.4)%. The increased aging sensitivity of µAl-7.5 is likely due to the reduced particle size yielding increased reactivity over the coarser µAl-30 (Table 2 and Table 3). The nAl-100 is more prone to aging, due to the increased SSA (Figure 3(c)). A nearly complete corruption of the original C_Ai is achieved in less than 30 hours. After 48 hours, the active metal content of the powder is (2.3 ± 0.3)% and the corresponding α_Ai-AsiO3 is (96.3 ± 0.9)%. The mass gain during the powder aging in a wet environment is initially due to the adsorption of H₂O on the particle surfaces and the following formation of hydrated species as Al(OH)₃ and/or AlO(OH).

Table 3 reports the TG reactivity parameters for the aged powders. Micron-sized Al powders show a general increase of the T_melt after aging. This is probably due to the initial corruption of the Al₂O₃ shell yielding Al+H₂O reaction, with the creation of hydrated species. These hydrated species feature a reduced passivation effect, thus yielding further C_Ai decrease (in turn implying a thickened shell surrounding the residual metal core). Hydrated species are dehydrated during the TG heating, leaving a relatively thick Al₂O₃ layer that, in turn, reduces the powder reactivity at slow heating rates (see Figure 4). For nAl-100, no significant reactivity changes are identified for the earlier phases of the aging (Table 2 and Table 3). Passing to the aging times of 24 and 72 hours, the main observed phenomenon is the specimen mass loss (see Table 3). The Δm Writer agrees with the mass loss limit due to Al(OH)₃ dehydration to Al₂O₃, as reported by Sato. For 72-hours aging, nAl-100 C_Ai is nearly completely consumed, and a low conversion to Al₂O₃ is achieved due to the shielding action exerted by the refractory shell produced after the dehydration of the species formed during the aging.

4. Conclusions and future developments

This work focuses on the analysis of the effects of accelerated aging on the reactivity of micron- and nano-
Figure 2  Accelerated aging: $C_A(t)$ and $a_{Al\rightarrow Al(OH)_3}(t)$ for (a) $\mu$Al-30, (b) $\mu$Al-7.5, and (c) nAl-100, all under D1 condition.

Figure 3  Accelerated aging: $C_A(t)$ and $a_{Al\rightarrow Al(OH)_3}(t)$ for (a) $\mu$Al-30, (b) $\mu$Al-7.5 and (c) nAl-100, all under H1 condition.
sized powders. No significant aging effects are noticed for powders stored at 333 K with RH < 10% for 14 days (see Figure 2). Considering the storage under humid conditions (H1), differences are highlighted between micron- and nano-sized powders. Micron-sized powders show similar $C_0(t)$ and $\alpha_{\text{Al}(\text{OH})_3}(t)$, with a step decrease of the active metal content, and a corresponding increase in the $\alpha_{\text{Al}2O3}$, after 7 days of storage (Figure 3). This suggests the existence of a threshold thickness for the hydrated species passivation action. For the tested μAl, this limiting thickness (calculated for $C_0$ (336 hours), Al(OH)3 density of 3080 kg m$^{-3}$, and the $D_{\text{Al}}$ values of the Table 1), is in the range 0.6–3.0 μm. The lower limit of this range exceeds the tested nAl size. The nAl-100 shows a weaker resistance to the humid environment. The powder $C_0$ decreases monotonically reaching limiting values of nearly 2 wt% in 72 hours. According to TG analyses and open literature data [14], the powder modifications are likely due to the formation of different aluminum hydroxide polymorphs (see $\Delta m_0$ and $T(\Delta m_0)$ in Table 3). The aging of the powders yields reduced Al$\rightarrow$Al$_2$O$_3$ conversion. Future developments of this work will focus on a deeper investigation of the thermal behavior of the aluminum powders for points of incipient change of the disperse system characteristics, and on an evaluation of the effects of higher heating rates on the thermal behavior of the materials.

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