

# Aluminum powders: aging effects on metal content and thermogravimetry reactivity

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Received: December 2, 2017 Accepted: September 14, 2018

## 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 ( $C_{Al}$ ) loss in nearly 30 hours ( $RH = 80\%$ ). Under the same condition, in 14 days of aging, the  $C_{Al}$  of micron-sized aluminum (30  $\mu\text{m}$ ) decreases from  $(99.1 \pm 0.2)\%$  to  $(86.8 \pm 0.9)\%$ .

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

## Nomenclature

$D_{32}$	surface-based mean particle diameter [nm]
$T_{\text{end},i}$	$i$ -th intense oxidation end temperature [K]
$T_{\text{onset},i}$	$i$ -th intense oxidation onset temperature [K]
$\alpha_{Al \rightarrow Al_2O_3}(T)$	Al $\rightarrow$ Al <sub>2</sub> O <sub>3</sub> conversion factor, $\Delta m(T)/(C_{Al} \cdot 0.89)$ [%]
$\alpha_{Al \rightarrow Al(OH)_3}(t)$	Al $\rightarrow$ Al(OH) <sub>3</sub> conversion factor, $\Delta m(t)/(C_{Al} \cdot 1.889)$ [%]
$\Delta m_0$	mass change due to desorption/dehydration [%]
$\Delta m_1$	mass change in the first oxidation step [%]
$\Delta m_{933K}$	mass change at 933 K [%]
$\Delta m_{1223K}$	mass change at 1223 K [%]

## 1. Introduction

Aluminum is a high density energetic material widely used in solid propellants and fuels for rocket propulsion<sup>1–6</sup>. Currently, commercial solid propellants are based on air-passivated micron-sized aluminum ( $\mu\text{Al}$ ) with size in the range 50–15  $\mu\text{m}$ . These powders are characterized by metal contents ( $C_{Al}$ ) typically higher than 95 wt%, and specific surface area (*SSA*) lower than 1  $\text{m}^2 \text{g}^{-1}$ . Nano-sized Al (nAl) features increased reactivity

over the conventional  $\mu\text{Al}$ <sup>1,4,6</sup>. In general, air-passivated nAl exhibits  $SSA \geq 10 \text{ m}^2 \text{g}^{-1}$ , and  $C_{Al} < 90 \text{ wt}\%$ <sup>1,6</sup>. 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<sup>7–12</sup>, 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  $\mu\text{Al}$  to nAl. The collected data show the aging effects on powder energetic content ( $C_{Al}$ ) 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 ( $\mu\text{Al}$ -30, and  $\mu\text{Al}$ -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

**Table 1** Initial characteristics of the tested  $\mu\text{Al}$  and  $\text{nAl}$  powders. The SSA-based diameter is evaluated as  $a_s = 6/(\rho_{\text{Al}} \cdot \text{SSA})$ , with  $\rho_{\text{Al}} = 2700 \text{ kg m}^{-3}$ .

Id.	Nominal size [nm]	SSA [ $\text{m}^2 \text{ g}^{-1}$ ]	$a_s$ [nm]	$D_{32}$ [nm]	$C_{\text{Al}}$ [wt%]
$\mu\text{Al-30}$	30000	< 0.1	> 22000	28900	$99.1 \pm 0.2$
$\mu\text{Al-7.5}$	7500	< 0.1	> 22000	4150	$95.3 \pm 0.2$
$\text{nAl-100}$	100	$12.6 \pm 0.1$	176	133	$85.7 \pm 0.6$

materials, respectively). The specific surface area was determined by  $\text{N}_2$  adsorption/desorption isotherms and the BET equation<sup>1)</sup>. The  $C_{\text{Al}}$  was evaluated by a volumetric method based on the  $\text{Al}+\text{H}_2\text{O}$  reaction<sup>1), 5), 6)</sup>. Thermogravimetry (TG) analyses were performed in air, with heating rate of  $10 \text{ K min}^{-1}$ . Powder reactivity was determined exploiting the parameters suggested by Ilyin *et al.*<sup>13)</sup>.

### 2.3 Aging conditions

The aging of the powders was studied under a temperature of 333 K, to accelerate the corruption process. Two different conditions of  $RH$  were considered to highlight the effects of the  $\text{H}_2\text{O}$  vapor concentration. In the dry environment D1 condition,  $RH < 10\%$  (dry air +  $\text{SiO}_2$ ), while in the humid environment H1 condition  $RH = (80.2 \pm 0.4)\%$  (saturated  $\text{H}_2\text{O}$  +  $\text{KCl}$  solution). Accelerated aging conditions were produced in sealed glass containers with internal volume of  $0.5 \text{ dm}^3$ . These vessels were prepared and stored at  $T = 333 \text{ K}$  for 24–48 hours, before the start of the experiments. Small amounts of powder (0.3–0.4 g) were inserted in glass weighting bottles with diameter of 30 mm. The (opened) weighting 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  $C_{\text{Al}}$  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  $D_{32}$  values in agreement with the nominal size. The  $\mu\text{Al-7.5}$  features  $D_{32} = 4150 \text{ nm}$ , due to a bimodal distribution with a small powder fraction (< 3.0 vol.%) of sub-micrometric size (400–1000 nm). The  $\text{nAl-100}$  SSA-based particle diameter<sup>13)</sup> ( $a_s$ ) shows a general agreement with the  $D_{32}$  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<sup>1)</sup>. TG traces for the non-isothermal

oxidation of  $\mu\text{Al-30}$ ,  $\mu\text{Al-7.5}$  and  $\text{nAl-100}$  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  $\gamma\text{-Al}_2\text{O}_3$  phase transition<sup>4)</sup>. The  $T_{\text{onset},1}$  shows no clear correlation with the powder size, as evidenced by the intense oxidation onset temperature for the  $\text{nAl-100}$  with respect to the  $\mu\text{Al-7.5}$ . 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  $\text{nAl-100}$  yields an increased reactivity over the  $\mu\text{Al}$ -counterparts, as testified by the  $\Delta m_{933\text{K}}$ ,  $\alpha_{\text{Al} \rightarrow \text{Al}_2\text{O}_3}$  (933 K) and  $\alpha_{\text{Al} \rightarrow \text{Al}_2\text{O}_3}$  (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  $\mu\text{Al}$  and  $\text{nAl}$  specimens (see Figure 2). The powder mass is nearly unchanged during a period of 14 days, independently from the powder dispersity. The relatively low  $\text{H}_2\text{O}$  content in the aging environment limits the corruption of the  $\text{Al}_2\text{O}_3$  shell (i.e., its transformation into hydrated species as  $\text{Al}(\text{OH})_3$ ). Over the 14 days aging period, the  $C_{\text{Al}}$  of  $\mu\text{Al-30}$  shows no decrease. Similarly, the active metal content of  $\mu\text{Al-7.5}$  shows values of  $(94.8 \pm 0.4)\%$  at 7 days and  $(94.2 \pm 0.6)\%$  at 14 days, being substantially unchanged. Active metal content of  $\text{nAl-100}$  after 14 days of storage at  $RH < 10\%$  is  $(85.6 \pm 0.3)\%$ . TG analyses show that after dry environment storage,  $\text{nAl-100}$  mass loss due to the adsorbed gas desorption is  $(-0.9 \pm 0.1)\%$ , while  $T_{\text{onset},1} = (857.5 \pm 0.1) \text{ K}$  and the conversion factor from  $\text{Al} \rightarrow \text{Al}_2\text{O}_3$  at 933 K and 1223 K are  $(38.7 \pm 0.2)\%$  and  $(84.8 \pm 0.6)\%$  respectively.

#### 3.2.2 Humid environment (H1)

For the H1 tests, the  $\text{Al} \rightarrow \text{Al}(\text{OH})_3$  conversion factor  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}(t) = \Delta m(t)/(C_{\text{Al}} \cdot 1.889)$  is defined as a function of the aging time ( $t$ ). The  $C_{\text{Al}}(t)$  and the  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}(t)$  are shown in Figure 3 for  $\mu\text{Al-30}$ ,  $\mu\text{Al-7.5}$  and  $\text{nAl-100}$ . Note that the  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}(t)$  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  $C_{\text{Al}}(t)$ . This is then followed by a stabilization of the metal content in time. The  $\mu\text{Al-30}$  shows a  $C_{\text{Al}}$  change from

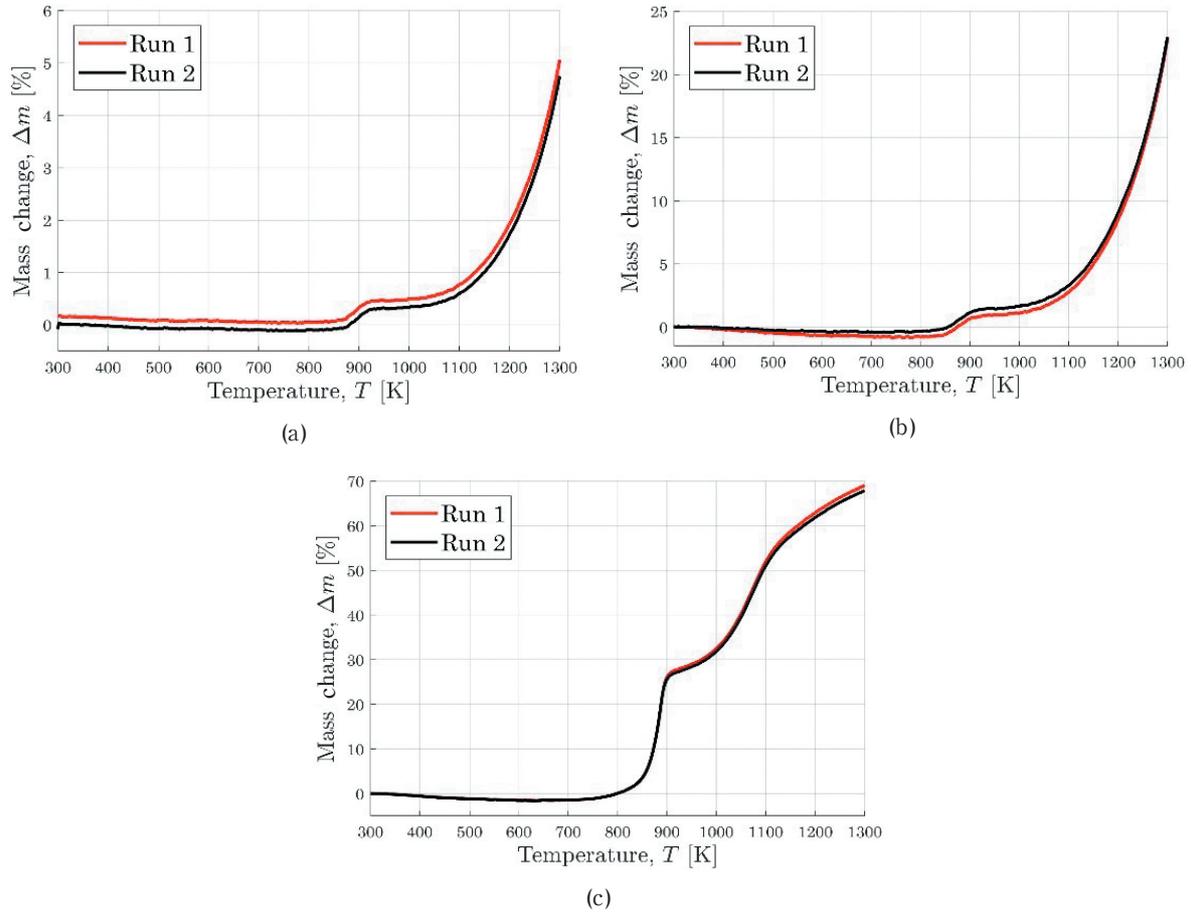


Figure 1 TG traces (air, 10 K min<sup>-1</sup>, 0.1 MPa) of fresh (a)  $\mu$ Al-30, (b)  $\mu$ Al-7.5, and (c) nAl-100.

Table 2 Fresh Al powder reactivity parameters (TG, 10 K min<sup>-1</sup>, air, 0.1 MPa).

	$\mu$ Al-30	$\mu$ Al-7.5	nAl-100
$\Delta m_0$ [%]	$-0.2 \pm 0.1$	$-0.6 \pm 0.3$	$-1.6 \pm 0.4$
$T(\Delta m_0)$ [K]	$782.7 \pm 2.1$	$741.2 \pm 0.7$	$663.4 \pm 1.9$
$T_{\text{onset},1}$ [K]	$865.0 \pm 0.3$	$842.5 \pm 0.5$	$856.1 \pm 0.2$
$\Delta m_1$ , [%]	$0.5 \pm 0.1$	$1.8 \pm 0.5$	$28.2 \pm 0.4$
$T_{\text{end},1}$ [K]	$915.3 \pm 0.6$	$905.2 \pm 0.4$	$898.4 \pm 0.5$
$\Delta m_{933\text{K}}$ [%]	$0.5 \pm 0.2$	$1.8 \pm 0.5$	$29.5 \pm 0.4$
$\alpha_{\text{Al} \rightarrow \text{Al}_2\text{O}_3}$ (933 K) [%]	$0.6 \pm 0.1$	$2.2 \pm 0.6$	$38.7 \pm 0.6$
$T_{\text{onset},2}$ [K]	$1224.2 \pm 0.4$	$1203.3 \pm 0.4$	$1014.9 \pm 0.5$
$T_{\text{end},2}$ [K]	NAv.	NAv.	NAv.
$\Delta m_{1223\text{K}}$ [%]	$2.5 \pm 0.2$	$11.6 \pm 0.5$	$65.6 \pm 0.8$
$\alpha_{\text{Al} \rightarrow \text{Al}_2\text{O}_3}$ (1223 K) [%]	$2.9 \pm 0.2$	$13.7 \pm 0.5$	$86.0 \pm 1.1$

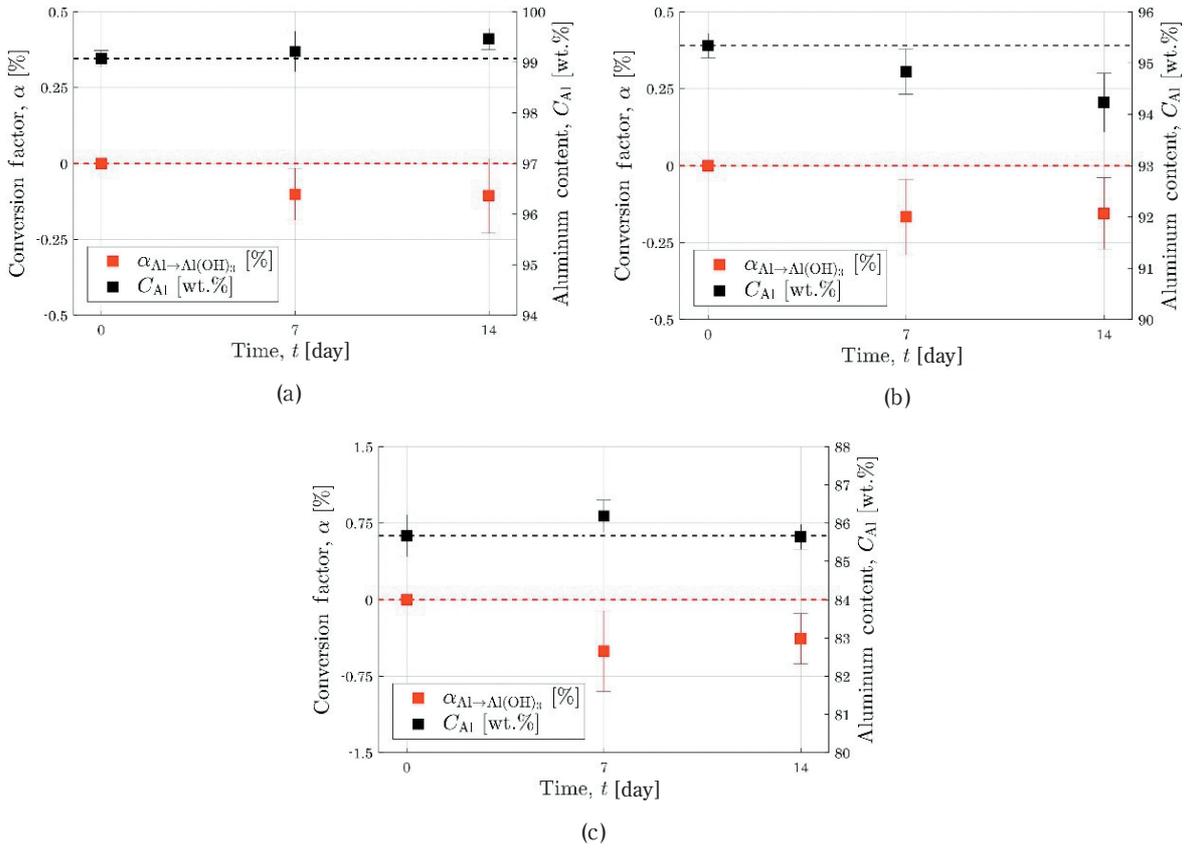
( $99.1 \pm 0.2$ )% to ( $86.8 \pm 0.9$ )%, with a  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}$  (14 days) = ( $4.7 \pm 0.2$ )%. The  $\mu$ Al-7.5 shows a similar behavior, with  $C_{\text{Al}}$  (7 days) = ( $58.1 \pm 0.8$ )%. This value is further decreased to ( $55.8 \pm 0.6$ )% for  $t = 14$  days. The  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}$  (14 days) is ( $21.3 \pm 1.4$ )%. The increased aging sensitivity of  $\mu$ Al-7.5 is likely due to the reduced particle size yielding increased reactivity over the coarser  $\mu$ Al-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  $C_{\text{Al}}$  is achieved in less than 30 hours. After 48 hours, the active metal content of the powder is ( $2.3 \pm 0.3$ )%, and the corresponding  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}$  is ( $96.3 \pm 0.9$ )%. The mass gain during the powder aging in a wet environment

is initially due to the adsorption of H<sub>2</sub>O on the particle surfaces and the following formation of hydrated species as Al(OH)<sub>3</sub> and/or AlO(OH).

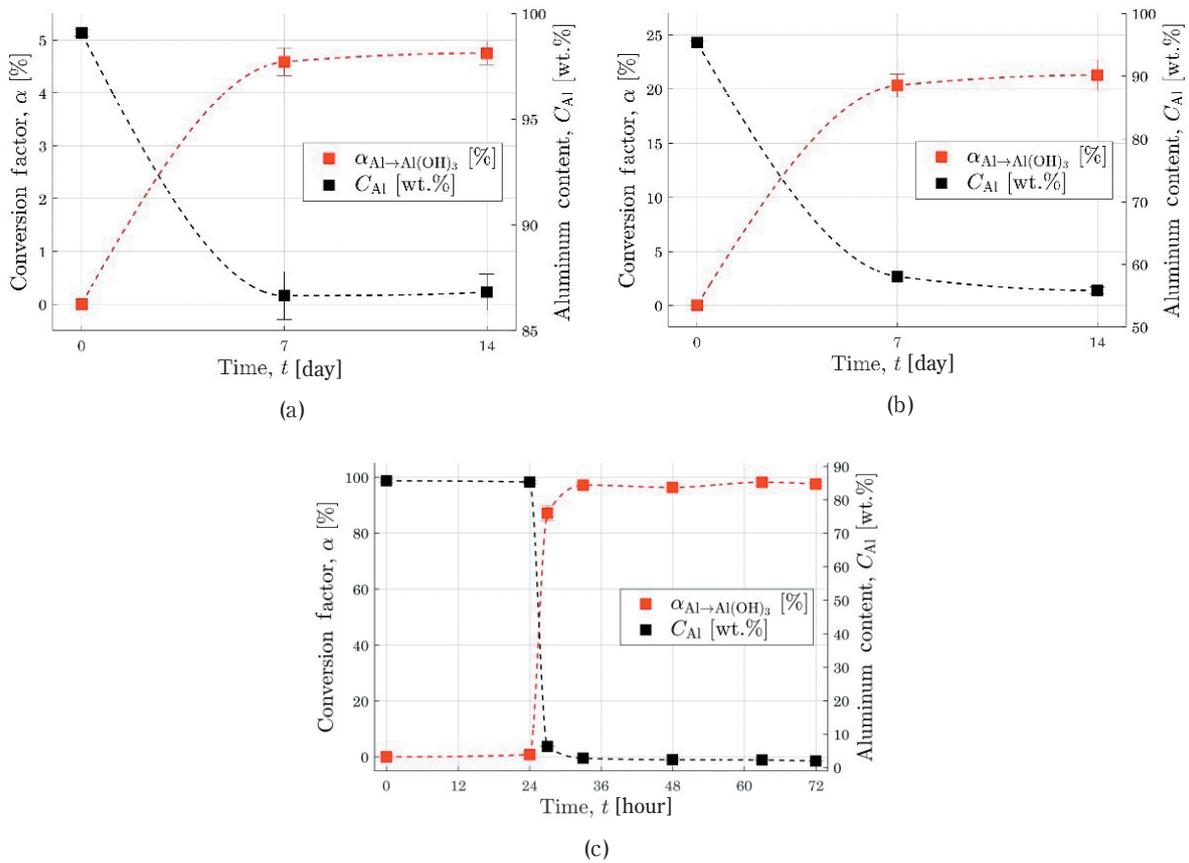
Table 3 reports the TG reactivity parameters for the aged powders. Micron-sized Al powders show a general increase of the  $T_{\text{onset},1}$  after aging. This is probably due to the initial corruption of the Al<sub>2</sub>O<sub>3</sub> shell yielding Al+H<sub>2</sub>O reaction, with the creation of hydrated species. These hydrated species feature a reduced passivation effect, thus yielding further  $C_{\text{Al}}$  decrease (in turn implying a thickened shell surrounding the residual metal core). Hydrated species are dehydrated during the TG heating<sup>14</sup>), leaving a relatively thick Al<sub>2</sub>O<sub>3</sub> 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  $\Delta m_0$  agrees with the mass loss limit due to Al(OH)<sub>3</sub> dehydration to Al<sub>2</sub>O<sub>3</sub>, as reported by Sato<sup>14</sup>). For 72-hours aging, nAl-100  $C_{\text{Al}}$  is nearly completely consumed, and a low conversion to Al<sub>2</sub>O<sub>3</sub> 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-



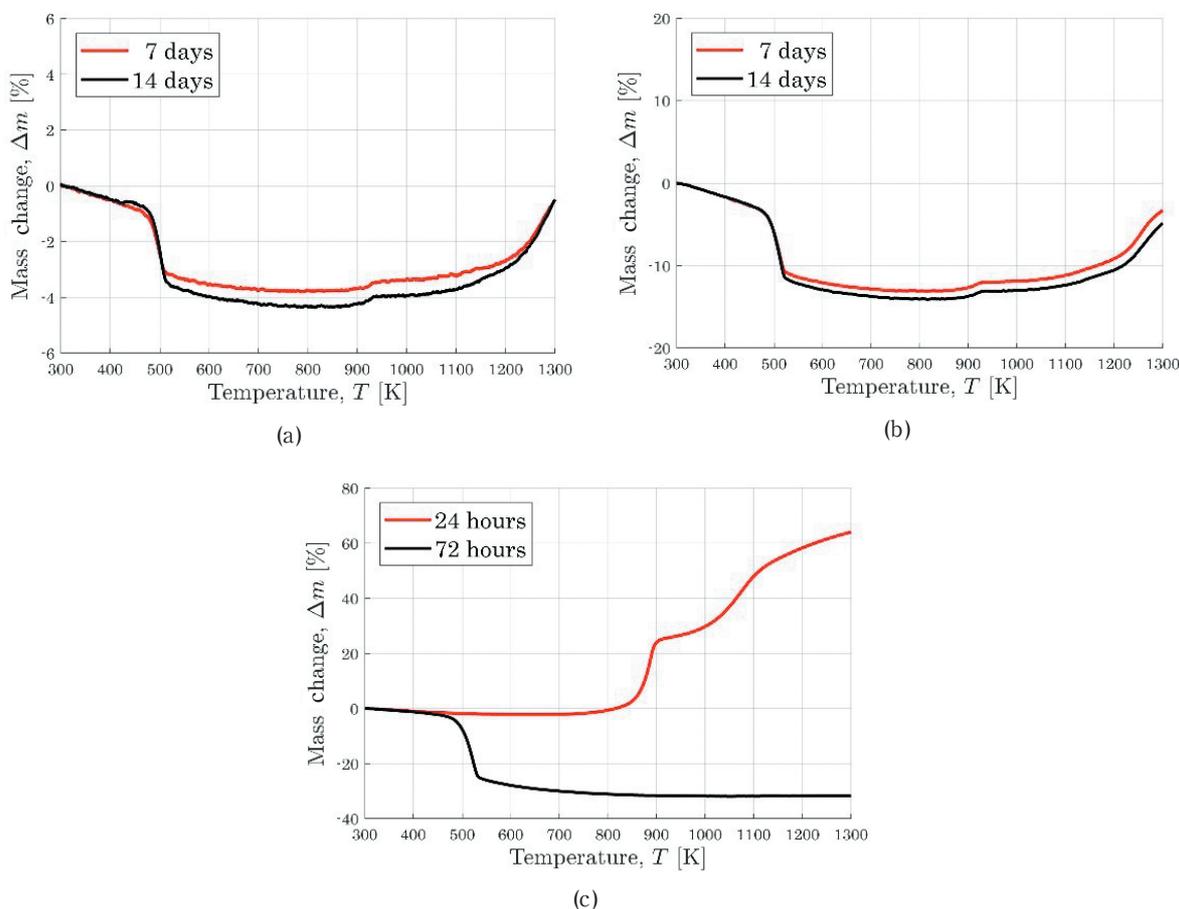
**Figure 2** Accelerated aging:  $C_{Al}(t)$  and  $\alpha_{Al \rightarrow Al(OH)_3}(t)$  for (a)  $\mu$ Al-30, (b)  $\mu$ Al-7.5, and (c) nAl-100, all under D1 condition.



**Figure 3** Accelerated aging:  $C_{Al}(t)$  and  $\alpha_{Al \rightarrow Al(OH)_3}(t)$  for (a)  $\mu$ Al-30, (b)  $\mu$ Al-7.5 and (c) nAl-100, all under H1 condition.

**Table 3** Reactivity parameters for TG analyses (air, 10 K min<sup>-1</sup>, 0.1 MPa) of tested Al powders during/after aging (H1 condition). Aging time: [day] for  $\mu$ Al, [hour] for nAl.

	Time [day], [hour]	$\Delta m_0$ [%]	$T_{\text{onset},1}$ [K]	$\alpha_{\text{Al} \rightarrow \text{Al}_2\text{O}_3}$ (933 K) [%]	$\alpha_{\text{Al} \rightarrow \text{Al}_2\text{O}_3}$ (1223 K) [%]
$\mu$ Al-30	14	$-4.3 \pm 0.1$	$895.9 \pm 0.6$	$0.6 \pm 0.3$	$2.4 \pm 0.6$
$\mu$ Al-7.5	14	$-13.9 \pm 0.2$	$884.3 \pm 0.3$	$1.9 \pm 0.6$	$8.6 \pm 0.6$
nAl-100	24	$-2.1 \pm 0.2$	$857.6 \pm 0.5$	$37.5 \pm 0.9$	$82.5 \pm 1.5$
	72	$-32.1 \pm 0.2$	Not identifiable	$10.0 \pm 0.1$	$10.6 \pm 0.1$

**Figure 4** TG traces (air, 10 K min<sup>-1</sup>, 0.1 MPa) of (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  $C_{\text{Al}}(t)$  and  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}(t)$ , with a step decrease of the active metal content, and a corresponding increase in the  $\alpha_{\text{Al} \rightarrow \text{Al}(\text{OH})_3}$  after 7 days of storage (Figure 3). This suggests the existence of a threshold thickness for the hydrated species passivation action. For the tested  $\mu$ Al, this limiting thickness (calculated<sup>1)</sup> for  $C_{\text{Al}}$  (336 hours),  $\text{Al}(\text{OH})_3$  density of 3080 kg m<sup>-3</sup>, and the  $D_{32}$  values of the Table 1), is in the range 0.6–3.0  $\mu\text{m}$ . The lower limit of this range exceeds the tested nAl size. The nAl-100 shows a weaker resistance to the humid environment. The powder  $C_{\text{Al}}$  decreases monotonically reaching limiting values of nearly 2 wt% in 72 hours. According to TG analyses and open literature data<sup>14)</sup>, 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  $\text{Al} \rightarrow \text{Al}_2\text{O}_3$  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.

### Acknowledgement

This work is partially financed by the GRAIL H2020 program (EU grant agreement no. 638719). The authors thank Dr. Gianluigi Marra (ENI, Centro Ricerche per le Energie Rinnovabili e l'Ambiente) for the helpful discussions.

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