Aging Effects on Nano-sized Aluminum Reactivity

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Abstract

Nano-sized Al (nAl) features high reactivity that, while desirable for effective energy conversion during the combustion, yields possible issues related to its storage. This paper investigates the ageing behavior of nAl under different relative humidity conditions (RH, from 80% to 10%) at the temperature of 333 K. Fresh and aged powders are characterized by electron microscopy, x-ray diffraction, and thermal analysis. The marked sensitivity of nAl (40 nm) to ageing is testified by a nearly full metal content (C_{Al}) loss in just 24 hours (RH = 80%). Under the same condition, conventional 30 µm-counterpart looses 13% of the original C_{Al} in 14 days.

Nomenclature

as	=	mean particle diameter from SSA, nm
a _{δ,Al2O3}	=	calculated oxide layer thickness, nm
ALEX	=	nAl produced by electrical explosion of wires (typically air-passivated)
C _{Al}	=	active Al content, wt%
CCP	=	condensed combustion products
D ₃₂	=	surface-based mean diameter, µm
D ₄₃	=	mass-based mean diameter, μm
DSC	=	differential scanning calorimetry
DTA	=	differential thermal analysis
nAl	=	nano-sized Al powder
nAl-40	=	nAl with nominal size of 40 nm
nAl-100	=	nAl with nominal size of 100 nm
μAl	=	micron-sized Al powder
μAl-7.5	=	μAl with nominal size of 7.5 μm
μAl-30	=	μAl with nominal size of 30 μm
RH	=	relative humidity, %
SEM	=	scanning electron microscopy
SSA	=	specific surface area, m ² /g
t	=	time
Т	=	temperature, K
$T_{end,i}$	=	i-th intense oxidation end temperature, K
T _{onset,i}	=	i-th intense oxidation onset temperature, K
TEM	=	transmission electron microscopy
TG	=	thermogravimetry
XRD	=	x-ray diffraction
$\alpha_{Al \rightarrow Al2O3}(T)$	=	Al \rightarrow Al ₂ O ₃ conversion factor at temperature T, $\Delta m(T)/(C_{Al} \cdot 0.89)$, %
$\alpha_{Al \rightarrow Al(OH)3}(t)$	=	Al \rightarrow Al(OH) ₃ conversion factor at time t, $\Delta m(t)/(C_{Al} \cdot 1.889)$, %
Δm_0	=	mass change due to adsorbed species desorption, %
Δm_1	=	mass change in the first oxidation step, %
Δm933K	=	mass change at 933 K, %
Δm_{1223K}	=	mass change at 1223 K, %

1. Introduction

Aluminum is a high density energetic material (enthalpy of oxidation in O_2 : 31.0 kJ/g_{Al}, 83.6 kJ/cm³_{Al}). This, together with the relatively low O₂-demand and the reduced cost, yields to the extensive use of Al in condensed energetic systems [1-3]. Typically, Al particles are passivated by air and present a layered structure with a metal core surrounded by an amorphous Al₂O₃ shell. The latter is purposely generated by the controlled powder exposure to a dry air environment during the production phase. The Al₂O₃ layer prevents the fast Al reaction with the surrounding environment at ambient conditions. The thickness of the oxide shell is primarily controlled by the diffusion of oxidizing species (in particular, O_2) toward the metal core. For temperatures in the range ambient to 673 K, the limiting thickness of this layer (4-5 nm) seems independent from powder morphology and size [4-6]. For T > 673 K, the oxide layer thickness and its crystalline structure change in the presence of O_2 [6]. Aluminum powders are widely used in solid propellants and fuels for rocket propulsion [7-9]. Currently, commercial propellants are based on air-passivated µAl. The key features of Al powders in the micron-sized range are high C_{Al} (typically higher than 95 wt%), and SSA usually lower than 1 m²/g. While the metal content grants a high theoretical energy content to the powder, the relatively low SSA yields limited reactivity (i.e., high ignition temperature [10]). Nano-sized Al powders feature increased reactivity over the conventional μ Al [11]. In general, air-passivated nAl shows SSA $\geq 10 \text{ m}^2/\text{g}$, and a reduced C_{Al} (< 90 wt%). While attractive in terms of the enhanced performance in a combustion environment, nAl high reactivity may yield issues related to ageing under storage. In particular, powders may lose C_{Al} during storage. As a consequence, the effects of their combustion are altered (i.e., reduced enthalpy release, different reaction mechanism). Table 1 shows the effects of powder C_{Al} decrease on the flame temperature (T_{fl}) and vacuum specific impulse (I_{s,vac}) of a typical aluminized commercial solid propellant based on ammonium perchlorate (AP, 68 wt%) and hydroxyl-terminated polybutadiene (HTPB, 14 wt%). In the propellant, the Al powder mass fraction is 18%. The propellant oxidizer to fuel ratio (O/F) results 2.125. The calculations are performed by NASA CEA code [12-13]. In the Table 1 data are evaluated considering different metal contents in the Al powder added to the propellant. The CAI is varied in the range 100 wt% (ideal case, assuming the absence of the Al₂O₃ layer) to 50 wt%. The C_{Al} reduction is achieved assuming that in the powder the remainder of the metal is its oxide (Al₂O₃). The same working hypotheses are used for the evaluation of the T_{fl} and I_{s,vac} in O₂ of HTPB + 10 wt% Al solid fuel formulation, for $2 \le O/F \le 4$ (see Figure 1). In this case, a O/F range is considered to provide an insight of the performance changes due to the oxidizer-to-fuel ratio shift [14]. In commercial solid propellants, high density energetic additives as µAl are added mainly to improve the specific impulse of the system (see Table 1), with a crucial role played by C_{Al}. In solid fuel formulations metal particles are exploited to augment the heat transfer from the flame zone to the condensed phase, with a higher importance of additive reactivity over the active metal content [8, 15-16]. The theoretical $I_{s,vac}$ for the metallized propellant formulations shows a strong dependence from the powder C_{Al} . Under the investigated conditions, nearly linear $T_{fl}(C_{Al})$ and $I_{s,vac}(C_{Al})$ trends are identified. A 10% decrease of the powder metal content yields a specific impulse decrease of nearly 2%. With a decrease of the C_Al from 100 wt% to 50 wt%, the $T_{\rm fl}$ of the investigated solid propellant decrease from 3382 K to 2909 K, while the theoretical vacuum specific impulse drops by 10.1%. Data reported in Figure 1 shows a minor performance dependence with respect to propellant compositions. When the powder C_{Al} decreases from 100 wt% to 50 wt%, the maximum T_{fl} in O₂ reduces from 3828 K to 3776 K, with a percent difference of 1.4%. The same aluminum content difference decreases the flame temperature of solid propellant formulations of 14%. The impact of the powder C_{Al} on Is,vac is stronger for solid propellants than for solid fuel formulations: the maximum vacuum specific impulse of HTPB + 10 wt% Al decreases from 352.2 s to 348.9 s (-0.9%, see Figure 1) for a C_{Al} change from 100 wt% to 50 wt%. The change in the material active metal content does not alter the mass fraction of condensed combustion products evaluated by the thermochemical equilibrium for both solid propellants and fuels. Nevertheless, the metal powder reactivity (not captured by the chemical composition analysis) plays a key role in the determination of burning rates of condensed materials, and on the formation of aggregates/agglomerates [2, 18-23]. In this respect, both initial particle size (µAl vs. nAl) and its ageing characteristics (i.e., surface composition and permeability) play a significant role [20-24]. Due to this, an investigation of the effects of ageing on the powder reactivity is of high relevance.

This paper investigates the accelerated ageing behavior of aluminum powders with various particle sizes and morphologies. The samples are stored under different relative humidity and temperature conditions. Tested powders range from conventional μ Al to nAl. All the tested powders are passivated by air. Implemented diagnostics include: SEM/TEM, XRD, C_{Al} determination, sample weight monitoring in time and reactivity analysis by TG. The collected information shows the ageing effects on powder energetic content (C_{Al}) and reactivity (low heating rate, TG).

Al Content in the Propellant, wt%	C _{Al} , wt%	T _{fl} , K	I _{s,vac} , S	ΔI _{s,vac,%} , %	
0 a	-	1372	239.1	-	
0^b	-	2890	287.4	-	
	100	3382	314.4	0.0	
	99	3376	313.8	-0.2	
	95	3349	311.5	-0.9	
10	90	3312	308.6	-1.8	
18	80	3229	302.6	-3.8	
	70	3133	296.2	-5.8	
	60	3026	289.5	-7.9	
	50	2909	282.6	-10.1	

Table 1: Theoretical performance of non-metalized/aluminized solid propellant formulations (NASA CEA Code, chamber pressure 7.0 MPa, expansion ratio 40, shifting equilibrium, HTPB heat of formation from [17]).

^{*a b*}Non-metallized formulation with oxidizer to fuel ratio of the metallized variant (O/F = 2.125): AP (68 wt%), HTPB (32 wt%).

^{*b*}Non-metallized formulation with O/F = 6.143, binder content is the same as per the metallized formulations (HTPB, 14 wt%), while the AP mass fraction is increased (86 wt%).

1.1 Literature Survey

Few open literature studies deal with the Al ageing process [25-29], while ageing effects (under non fully controlled/reported conditions) are observed in different publications [20,30-32]. This is likely because the widely used µAl shows a reduced sensitivity to storage, thanks to its low SSA values. Nano-sized Al features high SSA values, making it prone to ageing problems. This, together with the powder difficult dispersion down to the nanoscale and high volability, represent the biggest difficulty for an industrial application of nAl. Cliff et al. tested air passivated nAl $(C_{AI} = 88.2 \text{ wt\%}, \text{SSA} = 12.7 \text{ m}^2/\text{g})$, and a palmitic acid passivated variant of the same electro-exploded powder $(C_{AI} = 88.2 \text{ wt\%}, \text{SSA} = 12.7 \text{ m}^2/\text{g})$ = 86.1 wt%, SSA = 12.3 m²/g). A micron-sized aluminum powder with C_{AI} = 99.6 wt% and SSA = 1.27 m²/g was taken as a reference for the study. Powder samples with mass of 7 g were stored in covered Petri's dishes under environment with various accelerated ageing conditions. Specimens were stirred regularly to grant uniform exposure of the powder to the surrounding conditions. The more marked ageing effects were identified for RH = 75%, and temperatures of 313 K and 333 K. Under these conditions, the ALEX powder showed a C_{Al} drop to 4 wt% in a time span of 40 days. The Al degradation produced mainly Al(OH)₃ during the ageing process. The nAl powder passivated by palmitic acid showed a reduced sensitivity to wet environment ageing, with a CAI of 78% at the end of the 40 days of the experiment duration. Li et al. performed accelerated ageing tests under T = 303 K, for different RH levels (10-20%, 50-60%, and 80-90%) for a period of 8 weeks [26]. In the study, no details on the starting air-passivated nAl powders were given. High-resolution TEM images showed the growth of the passivation layer shell around the particles from 3 to 5 nm, because of the ageing process. DSC-TG analyses testified a non-clear trend of the oxidation behavior of the tested materials, though the two-step oxidation behavior of nAl was recognized over both fresh and aged specimens. A long-term study on nAl ageing (RH = 60-80%, T = 293-298 K) was performed by Nazarenko et al. [27]. In this study, nAl powders were stored for a period of at least 10 years. Non-isothermal oxidation of the powders showed an active behavior after the storage. In particular, ALEX produced in Ar revealed a reactivity similar to the one of fresh powders, with an overall heat release of 8.5 kJ/g, for a $C_{Al} = 71$ wt%. Pisharath et al. tested the accelerated aging behavior of air-passivated and functional organic silane-passivated nAl powders. Detailed x-ray photoelectron spectroscopy (XPS) and TG analyses evidenced the effective deposition of the chemical passivation layer, that promoted an improved ageing resistance than the pristine Al_2O_3 -shell [28]. Tests performed by Cerri et al. contrasted the nAl metal content loss in solid propellant formulations, showing a marked effect on the Al corruption [29].



Figure 1: Theoretical performance of HTPB + 10 wt% Al fuel formulation burning in O₂ effects of the powder C_{Al} on (a) T_{fl}(O/F) and (b) Is,vac(O/F) (NASA CEA Code, chamber pressure 7.0 MPa, expansion ratio 40 shifting equilibrium, HTPB heat of formation from [17], initial oxidizer temperature 90 K).

2. Materials and Experimental Methods

2.1 Tested Powders

Micron-sized powders (μ Al-30, and μ Al-7.5) are produced by AMG Alpoco (UK) [33]. The nAl powders are ALEX produced by electrical explosion of wires. The nAl-100 is produced by Advanced Powder Technology (APT) LLC (Russia) [34], while nAl-40 is supplied by US Nanomaterials (USA) [35].

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), while the SSA was determined by N_2 adsorption/desorption isotherms and the BET equation [36]. The C_{Al} is determined by a volumetric method based on the Al + H₂O reaction [3,11]. Crystalline phase materials are identified by XRD. Thermogravimetric analyses were performed in air, with heating rate of 10 K/min. Powder reactivity was determined exploiting the parameters suggested by Ilyin et al. [37].

2.3 Accelerated Ageing

Accelerated ageing was studied by inserting small amounts of powder (~ 1 g) in glass weighting bottles with diameters of 30 mm. The relatively low amount of material granted a uniform exposure to the test environment. The open weighting bottles were placed in small plastic jars and were then inserted in a pre-prepared sealed glass vessel containing the test environments (see Table 2). The plastic jar prevented the contact between the weighting bottles and the silica/salt solution. The sealed glass vessels were prepared and stored at the test temperature 24-48 hours before the start of the experiments. The RH ranges from < 10% (dry air condition) to (80.2 ± 0.4) %. A single temperature condition of 333 K is considered in the study.

Table 2: investigated aging conditions, dry and wet environments RH and temperature.

Condition Id.	Temperature, K	RH, %	Notes
Dry, D1	333	< 10%	Dry air environment, by SiO ₂
Humid, H1	333	$80.2\pm~0.4$	Saturated H ₂ O + KCl solution

3. Experimental Results

3.1 Initial Characterization

The tested air-passivated powders range from the micron- to the nano-sized scale, and are listed in the Table 3. The a_s and the alumina layer shell thickness, $a_{\delta,Al2O3}$, are calculated by the Eq. 1 and the Eq. 2, respectively

$$a_s = 6/(\rho_{Al}SSA)^{-1/2} \tag{1}$$

$$a_{\delta,Al2O3} = \frac{a_s}{2} - \left[\frac{\rho_{Al2O3} \cdot C_{Al} \cdot (a_s/2)^3}{\rho_{Al} \cdot (1 - C_{Al}) + \rho_{Al2O3} \cdot C_{Al}}\right]^{1/3}$$
(2)

considering aluminum and amorphous alumina densities ($\rho_{Al} = 2700 \text{ kg/m}^3$ and $\rho_{Al2O3} = 3050 \text{ kg/m}^3$ respectively).

Micron-sized powders feature low SSA values, due to the high mean particle size (see D_{43} and D_{32} values in Table 3). The relatively low C_{Al} of the μ Al-7.5 is due to a small volume fraction in the powder lying in the sub-micrometric range. The relatively high particle size and the C_{Al} of the micron-sized powders, yield non-physical results for the $a_{\delta,Al2O3}$, that is therefore non-reported in the Table 3. Nano-sized particles show high SSA and reduced a_s . Considering the C_{Al} the alumina shell thickness result in the range 3-4 nm. The a_s of the nAl-100 results nearly doubled with respect to the nAl-40. XRD analyses performed on the powders revealed metallic Al as the unique crystalline phase in the materials.

Scanning electron microscope image of the μ Al-30 are shown in Figure 2, while the SEM of the nano-sized powders are reported in the Figure 3. Figure 4 shows the TEM images of nAl-100 and nAl-40. While μ Al-30 features some non-spherical granules, SEM and TEM images of the nAl powders show a relatively uniform circular shape of the particles (with few exceptions in the nAl-40, see Figure 4). This grants a relatively high confidence on the a_s and $a_{\delta,Al2O3}$ data presented in the Table 3. Finally, TG traces for the non-isothermal oxidation of the powders are reported in the Figure 5, while reactivity parameters for the non-isothermal oxidation are presented in the Table 4. The nAl powders show a two-step reaction process, with a first intense oxidation onset before the Al melting temperature (933 K) [11]. The T_{onset,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 μ Al-7.5. The increased SSA of nAl-100 and nAl-40 yields an increased reactivity over the μ Al-counterparts, as testified by the $\alpha_{Al\to Al2O3}$ (933 K) and $\alpha_{Al\to Al2O3}$ (1223 K) values. The incomplete Al conversion in Al₂O₃ during the TG runs is testified by both $\alpha_{Al\to Al2O3}$ limiting values and the absence of an ending point for the second intense oxidation step.

Table 3: initial characteristics of the tested μ Al and nAl powders. D₄₃, D₃₂ and C_{Al} are average results from three tests. The confidence interval of C_{Al} is standard deviation.

Powder Id.	Nominal Size, nm	SSA, m²/g	as, Eq. 1 nm	D43, μm	D32, μm	CAI, wt%	аъ,A12O3, Eq. 2, nm
μA1-30	30000	< 0.1	>22000	44200 ^b	28900 ^b	99.1 ± 0.2	NAv.
μAl-7.5	7500	< 0.1	>22000	6600 ^b	4150 ^b	95.3 ± 0.2	NAv.
nAl-100	100	12.6 ± 0.1	176	138 ^c	133 ^c	85.7 ± 0.6	3.9
nAl-40	40	24.5 ± 0.1	90.7	NAv.	NAv.	77.1 ± 0.5	3.4

^a Measured by Malvern Mastersizer 2000 (dry dispersion unit).

^b Measured by Malvern Mastersizer 2000 (liquid dispersion unit).



Figure 2: SEM of the µAl-30, note the presence of large, non-spherical granules and the absence of particle clustering.

3.2 Aging Effects

Dry Environment

Tests performed under RH < 10% show a similar trend between μ Al and nAl powders. The powder mass is nearly unchanged during a period of 14 days, independently from the powder dispersity. This is due to a limited gaseous species adsorption on the powder surface, and Al core corruption during the storage. The relatively low H₂O content in the aging environment limits the corruption of the Al₂O₃ shell, and its possible transformation into hydrated species [as Al(OH)₃]. Under the investigated conditions, the alumina layer shows an effective passivation action on the Al. Over the 14 days aging period, the C_{Al} of μ Al-30 shows no decreases. Similarly, the active metal content of μ Al-7.5 changes from (95.3 ± 0.2)% to (94.2 ± 0.9)%. The nAl-100 shows no C_{Al} change, while for the nAl-40, the faint active aluminum content change is hidden by the error bars [from (77.1 ± 0.5)%) to (76.5 ± 0.8)]. The 14 days aging produces no influences on the nAl T_{onset,1} and Al \rightarrow Al₂O₃ conversion factor as shown in Table 5. This result suggests the presence of a threshold condition for the Al content corruption by oxidizing species as the H₂O vapor and the good protective action of the Al₂O₃ passivation layer.



Figure 3: SEM of (a, b) nAl-100 and (c,d) nAl-40. The marked clustering tendency of nanoparticles is evident. Particle size distribution of nAl-100 appear relatively uniform, with few (if any) particles with size in the submicrometric range, while larger granules are observed in nAl-40, see (d).



Figure 4: TEM of (a) nAl-100 and (b) nAl-40. Note the core-shell structure typical of air-passivated Al powders, and the relatively uniformity of the Al₂O₃ shell thickness. Few non-spherical elements are recognized in the nAl-40 powder (black arrows), as well as relatively large particles (white arrows).



Figure 5: TG traces (air, 10 K/min, 0.1 MPa) of (a) $\mu Al\text{-}7.5$ and (b) nAl-100.

Table 4: Fresh Al powder reactivity parameters (TG, 10 K/min, air, 0.1 MPa). Interval of confidence for the tw	wo
performed runs defined by standard deviation.	

	μAl-30	μAl-7.5	nAl-100	nAl-40
$\Delta m_0, \%$	-0.2 ± 0.1	-0.6 ± 0.3	-1.6 ± 0.4	-2.2 ± 0.2
Τ(Δm ₀), Κ	782.7 ± 2.1	741.2 ± 0.7	663.4 ± 1.9	608.5 ± 0.3
T _{onset,1} , K	865.0 ± 0.3	842.5 ± 0.5	856.1 ± 0.2	816.5 ± 1.0
Δm_1 , %	0.5 ± 1.8	1.8 ± 0.7	28.2 ± 0.4	28.8 ± 0.4
T _{end,1} , K	915.3 ± 0.6	905.2 ± 0.4	898.4 ± 0.5	866.7 ± 0.5
Δm ₉₃₃ , %	0.5 ± 0.2	1.8 ± 0.7	29.5 ± 0.4	31.6 ± 0.3
$\alpha_{\rm Al \rightarrow Al2O3}(T=933~K)$	0.6 ± 0.1	2.2 ± 0.8	38.7 ± 0.7	46.1 ± 0.6
T _{onset,2} , K	1224.2 ± 0.4	1203.3 ± 0.4	1014.9 ± 0.5	992.8 ± 2.7
T _{end,2} , K	NAv.	NAv.	NAv.	NAv.
Δm _{1223K} , %	2.5 ± 0.2	11.6 ± 0.6	65.6 ± 0.8	62.4 ± 0.5
$\alpha_{Al \rightarrow Al2O3}(T = 1223 \text{ K})$	2.9 ± 0.2	13.7 ± 0.8	86 ± 1.4	90.9 ± 1.2

Table 5: relevant reactivity parameters for 14 days-aging test in dry environment (D1 condition).

	nAl-100	nAl-40
C _{Al}	85.6 ± 0.5	76.5 ± 0.8
Δm_0 , %	-0.9 ± 0.1	-2.9 ± 0.3
Tonset,1, K	857.5 ± 0.1	817.5 ± 0.5
$\alpha_{Al \rightarrow Al2O3}(T = 933 \text{ K})$	38.7 ± 0.3	46.2 ± 0.7
$\alpha_{Al \rightarrow Al2O3}(T = 1223 \text{ K})$	84.9 ± 0.7	88.3 ± 1.4

Humid Environment

The humid condition created by the use of a KCl-saturated H₂O solution was investigated at 333 K (see Table 2). For the considered tests, the Al \rightarrow Al(OH)₃ conversion factor is defined as a function of the ageing time , according to the Eq. 3

$$\alpha_{\text{Al} \to \text{Al}(\text{OH})3}(t) = \Delta m(t) / (C_{Al} \cdot 1.889)$$
(3)

The specimen mass change during the ageing, the $C_{Al}(t)$ and the $\alpha_{Al \rightarrow Al(OH)3}(t)$ are shown in Figure 6 for the coarser micron-sized Al and the more disperse investigated nAl. Note that the $\alpha_{Al \rightarrow Al(OH)3}(t)$ reflects the mass increase behaviors of the tested powders, while data interpolating lines are reported only to improve the readability of the images. The powder SSA shows an influence on the powder ageing: as shown in Figure 6a and Figure 6b, micronsized powders show an initial decrease of the $C_{AI}(t)$, and a corresponding specimen mass increase. After 7 days (168 hrs.), the decreasing behavior disappears, and both the active metal content and the sample mass values show no further changes till the end of the tests. The μ Al-30 exhibits a C_{Al} change from (99.1 \pm 0.2)% to (86.8 \pm 0.8)%, with a maximum mass increase of $(8.9 \pm 0.4)\%$ at 14 days. The final $\alpha_{Al \rightarrow Al(OH)3}$ for this powder is $(4.7 \pm 0.2)\%$. The μ Al-7.5 shows a similar behavior, with C_{Al} at 7 days of aging of (58.1 ± 0.8)%, that is further decreased to (55.8 ± 0.6)% for t = 14 days (336 hrs.). The final mass gain for this powder is $(38.4 \pm 2.5)\%$, with $\alpha_{Al \rightarrow Al(OH)3} = (21.3 \pm 1.4)\%$. The increased ageing sensitivity of the finer micron-sized powder is probably due to the presence of a sub-micrometric fraction of particles yielding a higher reactivity than the µAl-30. High SSA powders (nAl-100 and nAl-40) are more prone to aging, as testified by the data presented in the Figure 6c and in the Figure 6d. Both the nano-sized Al powders show a nearly complete C_{Al} corruption under the investigated conditions. For nAl-100, the reaching of a reduction of 50% of the active metal content requires less than 30 hrs. Under the investigated conditions nAl-100 CAl is nearly unchanged in the first 24 hrs., and then reaches a value of $(6.2 \pm 0.2)\%$ for t = 27 hrs. After 48 hrs., the active metal content of the powder is $(2.3 \pm 0.5)\%$, and the mass change has reached its plateau value at 156% $[\alpha_{Al \rightarrow Al(OH)3} = (96.3 \pm 0.9)\%]$. The ageing rate for the nA1-40 is increased with respect to the nA1-100. The whole CA1 corruption process requires less than 24 hrs., with the active metal content dropping from $(72.7 \pm 1.4)\%$ to $(6.7 \pm 0.2)\%$ in a time interval of 9 hrs. (see Figure 6c). The final $\alpha_{A1 \rightarrow A1(OH)3}$ of the nAl-40 results (97.3 ± 1.3)%.



Figure 6: Evolution in time during accelerated aging of $\Delta m(t)$, $C_{Al}(t)$ and $\alpha_{Al \rightarrow Al(OH)3}(t)$ for (a, b) μ Al-30 and (c, d) nAl-40 (H1 condition). Interval of confidence is defined by standard deviation.

The mass gain during the powder ageing in a wet environment is due to the adsorption of H_2O on the particle surfaces and the following formation of hydrated species as $Al(OH)_3$ and AlO(OH). The phenomenon results more intense for powders with high SSA. The presence of crystalline aluminum oxides and hydroxides was investigated by XRD. Achieved results are reported in Table 6 and in Table 7 for micron- and nano-sized powders, respectively.

	Time,	Time, Al,		Al(OH) ₃ , %		
	days	% -	Bayerite	Boehmite	Nordstrandite	
	0	100	-	-	-	
μAI-30	7	96.9	2.8	-	0.3	
	0	100	-	-	-	
μAl-7.5	7	71.9	22.3	-	5.8	

Table 6: XRD results for µAl-30 and µAl-7.5 during aging (H1 condition).

Table 7: XRD results for nAl-100 and nAl-40 during aging (H1 condition).

	Time,	Al,	Al(OH)3, %		
	hours	%	Bayerite	Boehmite	Nordstrandite
	0	100	-	-	-
nAl-100	36	4.3	59.2	24.2	12.3
	72	2.7	68.2	22.0	7.1
n 41 40	0	100	-	-	-
nAl-40	24	3.0	51.9	38.2	6.9

The crystallographic data evidence the formation of hydrated oxides on the surface of the Al powders. Considering, by mass, the presence of the recognized Al(OH)₃ polymorphs (bayerite, boehmite, and nordstrandite) the XRD result show a good qualitative agreement with the achieved aging mass changes (see Figure 6). Under the investigated conditions, no boehmite was identified in the micron-sized Al corruption products, with this aluminum hydroxide polymorph that was identified only for the nAl-100 and nAl-40. The composition changes yield modifications in the morphology of the particles of the powders. In particular, the SEM images reported in Figure 7 testify the marked clustering tendency of the aged powders. Due to the granules alteration in the powder, yielding large sizes and thicknesses, no TEM images could be captured for the aged nAl specimens.

Table 8: reactivity parameters for TG analyses (air, 10 K/min, 0.1 MPa) of µAl-30 and µAl-30 during aging (H1 condition). Interval of confidence is defined by standard deviation over the two performed runs.

	Time, days	Δm_0 , %	Tonset,1, K	$\alpha_{A1 \rightarrow A1203}(933 \text{ K})^a, \%$	$\alpha_{A1 \to A1203}(1223 \text{ K})^{a}, \%$
μAl-7.5	24	$-13.1 \pm 0.0(4)$	884.4 ± 1.9	2.1 ± 0.1	9.1 ± 0.3
·	14	-13.9 ± 0.2	884.3 ± 1.9	1.9 ± 0.6	8.6 ± 0.6

^{*a*} Based on the C_{Al} from the volumetric analysis of the Al + H₂O reaction.



Figure 7: SEM images of aged samples (a) μ Al-30 (7 days), (b) nAl-100 (30 hrs.) and (b) nAl-40 (7 hrs.). Note the change in powder appearance with respect to the SEM images of Figure 3.

Table 9: reactivity parameters for TG analyses (air, 10 K/min, 0.1 MPa) of nAl-100 and nAl- 40 during aging (H
condition). Interval of confidence is defined by standard deviation over the two performed runs.

	Time, hours	$\Delta m_0, \%$	Tonset,1, K	$\alpha_{Al \rightarrow Al2O3}(933 \ K)^a, \%$	$\alpha_{Al \rightarrow Al2O3}(1223 \ K)^a, \%$
	24	-2.1 ± 0.2	857.6 ± 0.5	37.5 ± 0.9	82.5 ± 1.6
nAl-100	27	-30.2 ± 0.5	860.7 ± 0.4	$10.9 \pm {}^{b}$	38.2 ± 14.8
	72	-32.1 ± 0.2	NAv.	$10.6 \pm {}^{b}$	$10.6 \pm {}^{b}$
nAl-40	7	-9.6 ± 0.2	814.3 ± 0.2	47.1 ± 1.0	87.0 ± 2.5
	24	$-31.8 \pm 0.0(3)$	NAv.	9.7 ± 1.9	9.7 ± 2.4

^{*a*} Based on the C_{Al} from the volumetric analysis of the Al + H₂O reaction.

^b Wide interval of confidence, with standard deviation exceeding the average datum value.

Table 8 and Table 9 report the reactivity parameters for low temperature oxidation of aged micron- and nano-sized powders. For the micrometric powders, only μ Al-7.5 is considered, since the coarser 30 μ m powder showed high scattering of the thermal traces. The μ Al-7.5 exhibits a similar behavior (see Table 4 and Table 8). For this powder, the $\alpha_{Al \rightarrow Al2O3}(1223 \text{ K})$ shows a reduction from the fresh material value of $(13.7 \pm 0.8)\%$ to $(8.6 \pm 0.6)\%$ for the 14 days

aged material. This reactivity reduction of the micron-sized powders show a similarity with the $\alpha_{Al \rightarrow Al(OH)3}(t)$ where the initial powder reactivity is limited by the hydroxide layer build-up (Figure 6a and Figure 6b).

For nano-sized aluminum powders, no significant reactivity changes are identified for the earlier phases of the ageing (Table 9). After 24 hours of ageing, the nAl-100 features an increase in the initial mass loss [from $(-1.6 \pm 0.4)\%$ to $(-2.1 \pm 0.2)\%$], while the onset initial temperature shows a non-relevant shift. The $\alpha_{Al \rightarrow Al2O3}(1223 \text{ K})$ of the powder shows a decrease from the initial value of $(86.0 \pm 1.4)\%$ to $(82.5 \pm 1.6)\%$ after 24 hours of ageing. This result is caused by a minor reactivity loss in both the first and the second oxidation stages of the powder. Passing to the ageing times of 27 and 72 hours, the main phenomenon observed is the specimen mass loss, that reaches a nearly plateau condition (see Table 9). The latter Δm_0 agree with the mass loss limit due to $Al(OH)_3$ dehydration to Al_2O_3 (i.e., -34.6%) as reported by Sato [38]. A similar behavior is observed for the nAl-40. Also in this case, the powder aged for 7 hrs. shows as the main effect a mass loss, without alterations of the intense oxidation onset temperature. For the longest ageing time considered in the study (72 hrs. for nAl-100, and 24 hrs. for nAl-40), the nearly complete metal content consumption implies a loss of the identification of the intense oxidation onset temperature, and a low conversion of the Al to Al_2O_3 , due to the shielding action exerted by the refractory shell produced during the storage.

4. Conclusions and Future Developments

In this work, the effects of accelerated aging on the reactivity of micron- and nano-sized powders was investigated. Two different conditions were considered, D1 (RH < 10%, 333 K) and H1 [RH = (80.2 ± 0.4) %]. The starting characteristics of the tested powders are reported in Table 3. The aging behavior of the materials was investigated considering the evolution in time of the active metal content, and of the reactivity parameters from non-isothermal oxidation (TG) \Box [37]. Scanning and transmission electron microscope images of the powders were captured during the storage process. Crystalline phases were identified by XRD analyses.

The aging in dry environment (D1 condition) showed no marked effects on the powders, over a period of 14 days (see Table 5). This was due to the low RH, granting a slow interaction between the powders occurring (eventually) over storage times longer than the one considered in the study. Considering the storage under humid conditions (H1), differences were highlighted between micron- and nano-sized powders. Both μ Al-30 and μ Al-7.5 show similar C_{Al}(t) and $\alpha_{Al\to Al(OH)3}(t)$, with a step decrease of the active metal content (and a corresponding increase in the conversion factor) after 7 days of storage, see Figure 6a and Figure 6b. This trend is lost with the nano-sized powders, whose C_{Al} decreases monotonically reaching limiting values of nearly 2 wt% in 72 hours (nAl-100), and 24 hours (nAl-40). The powder modifications are mainly due to the formation of different aluminum hydroxide polymorphs (see Table 6 and Table 7). The ageing of the powders yields reduced Al \rightarrow Al₂O₃, conversion, while no significant shifts were noted for the first intense oxidation onset. The aging process produces a marked clustering of the powders and alterations in the morphology of the particles (see Figure 7). Under the investigated conditions, the ageing of the powders produced no influence of their reactivity, as suggested in some open-literature publication for nAl-loaded propellants (i.e., nanopowder reactivity at heating rates) [20]. Currently, further investigations on RH level/and storage time effects are in progress by this research team.

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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