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# Thermochimica Acta



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# Demonstrating an altered metal oxidation reaction mechanism correlated with variations in surface energy



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#### ARTICLE INFO

Keywords: Metal powder Surface energy Combustion control Solid fuels Power generation

# ABSTRACT

Thermal processing of powder media such as annealing and quenching alters particle surface properties and can influence the powder's reactivity. In this study, thermogravimetric analysis (TGA) was performed with microsized (4  $\mu$ m characteristic particle diameter) aluminum (Al) powder. Two powders were examined, namely, untreated Al (UN Al), i.e., procured from the manufacturer, compared with thermally processed Al by annealing and quenching (i.e., called super-quenched aluminum, SQ Al). TGA experiments were designed to compare the rate of oxidation of both materials. A new data processing technique was introduced that allows for a direct demonstration of altered reactivity by comparing the sample behavior during heating and cooling. The approach analyzes a normalized derivate drop of mass gain data throughout a programmed heating and cooling cycle depending on particle exposure time to oxygen at select temperatures. Results clearly confirm a difference between SQ Al and UN Al at temperatures around 600 °C, i.e., just below the Al melting temperature. The powders were also characterized using inverse gas chromatography (iGC) that showed a substantially higher surface energy of UN Al. Based on the experimental results, there is a correlation between Al reactivity and particle surface energy that substantiates recent observations of two different modes of Al particle combustion. Particle surface energy can be controlled to affect the mechanism for metal oxidation thereby affecting the rate of metal combustion.

# 1. Introduction

The chemical potential energy stored in a metal particle has an upper yield limit. For aluminum powder the theoretical maximum for aluminum oxidation is 31 kJ/g [1]. In applications, there are two important criteria for using metal powders to generate energy. The first is to harness all the potential chemical energy available and avoid leaving unburned, wasted fuel that results in decreased efficiency. The second criterium is more focused on the rate of energy generation because the timed release of energy contributes to the potential power available from metal oxidation. This study is designed to assess physical properties that influence reaction mechanisms and ultimately the rate of energy generation.

The burn times of single Al particles have been studied extensively [2–4]. A recent graphic summarizing years of burn time data collection for Al particles is shown by Sundaram et al. [3]. Once the nominal

particle diameter reduces from about 10  $\mu$ m, an inflection in the trend of burn time reduction with particle diameter is observed. Recently, two different regimes of aluminum (Al) particle combustion with two different burn times at a given particle diameter were experimentally observed [5]. Combustion of thermally processed (annealed and quenched) Al powder (called super-quenched aluminum, SQ Al) preferentially occurs in the fast mode (a shorter burn time), while untreated Al (called UN Al) mostly burns in the slow mode (a longer burn time).

Beyond burn times, different combustion regimes also resulted in different morphologies of final combustion products. A greater amount of nano-oxides is observed in the product residue recovered from SQ Al combustion compared with UN Al [6]. Combustion of SQ Al is also characterized by higher radiant fluxes compared with UN Al [6]. Both the variations in nano-oxide concentration and higher radiant fluxes resulting from SQ Al indicate differences in reaction mechanisms that control the rate of energy release.

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https://doi.org/10.1016/j.tca.2023.179521

Received 24 March 2023; Received in revised form 25 April 2023; Accepted 4 May 2023 Available online 5 May 2023 0040-6031/© 2023 Elsevier B.V. All rights reserved. While there is a measurable distinction in combustion of SQ Al and UN Al particles, an explanation for their differences requires further analysis. Moreover, revisiting fundamentals of the standard models [1–4] describing the Al combustion process is essential. Current combustion models try to predict how the burn time depends on the particle diameter and do not allow for two different times at a given particle size as has been directly observed using SQ Al compared with UN Al. Besides its fundamental importance, the discovery of different combustion regimes of Al particles has implications to energetic applications such as ordnance and propulsion technologies, in which the particle burn times and radiant fluxes govern heat exchange, and therefore, the system performance.

A logical way to address the puzzle related to different burn times for the same particle size of UN Al and SQ Al powders should be split into two parts. The first part should analyze the physical parameters that are different in the two materials because those parameters could be responsible for the varied burn times. The second part should focus on particle combustion modeling because developing an analytical model could provide an explanation for different combustion regimes.

A metal particle combustion concept that allows for two different regimes has been recently introduced [7]. In that discussed concept, the fast regime is common vapor-phase combustion with aluminum vapor reacting with oxygen gas in a reaction zone surrounding a metal particle. The slow combustion regime is realized via surface oxidation of aluminum followed by evaporation of metal suboxides. The essential condition of the slow regime is the existence of a layer of the aluminum oxide on the surface of a burning particle. An oxide layer of sufficient thickness should appear before the ignition onset that favors the slow combustion regime.

Although the concept needs to be further detailed, one theory is that UN Al and SQ Al may generate oxide films with different thicknesses at the pre-ignition stage. A hypothesis is that UN Al and SQ Al can arrive at ignition with the oxide film of different thicknesses and provide conditions that favor either slow combustion (i.e., UN Al with a thicker film) or fast combustion (i.e., SQ Al with a thinner film). The latter means that the pre-ignition reactivity of UN Al is higher than SQ Al, as required to produce a thicker oxide film on UN Al. Higher pre-ignition reactivity will lead to UN Al exhibiting stronger oxidation at low temperatures.

Pre-ignition reactivity can be resolved using thermal equilibrium analysis techniques. In the current paper, thermogravimetric analysis (TGA) was performed to directly demonstrate that more significant UN Al oxidation occurs at low temperatures compared to SQ Al. We show a data processing approach that eliminates possible experimental uncertainties commonly inherent for absolute measurements in order to distinguish a different amount of oxide accumulated on the two metal powders under identical conditions. The method is based on comparing rates of the sample mass gain during heating and cooling. Besides its importance for the particular problem explored in the current paper, the suggested data processing methodology could be useful for further advancing the TGA capabilities.

Variations in particle reactivity experimentally observed are linked to surface energy characterized using inverse gas chromatography (iGC). A higher surface energy of UN Al is shown to correspond to higher reactivity at low temperatures. Higher reactivity at low temperatures explains why more surface reactions with UN Al ultimately lead to a thicker pre-ignition oxide film yielding its burning in the slow regime.

### 2. Material and methods

The Al powder was supplied by Alfa Aesar (MA, USA) with a characteristic Al particle diameter of 4  $\mu$ m. Two powders were used in the experiments. The first was untreated, as-received powder, UN Al. The second was thermally processed and identified as super-quenched, SQ Al. The thermally processed powder has been detailed previously [6,8] but is summarized here. The Al powder was annealed to 320 °C and held for 10 min. After annealing, the powder was quenched rapidly using a prescribed powder metallurgical technique detailed in [6,8]. During the thermal processing, Al powder was kept in the sealed container. The material properties of both powders were well-characterized in our previous work [8]. The major physical parameter found different in these powders until now is their stress, which is an order of magnitude higher in SQ AI [8].

The powder materials were also demonstrated to behave differently in energetic applications [8–11] including the slower combustion of UN Al compared to preferential combustion of SQ Al in the fast regime [5,6]. Previous results that summarize particle properties are presented in Supplementary Information in Table S1. In the current paper, iGC and TGA are used to characterize and further link the powder surface energies and reactivities. Both iGC and TGA data combined together have not previously been investigated for SQ Al compared with UN Al but have potential to reveal key physical variations that contribute toward describing reaction dynamics.

An iGC Surface Energy Analyzer, SEA (Surface Measurement Systems, Alperton, UK) was used for powder measurements and the data were analyzed using SEA Analysis Software. Detailed methodology and results processing have been described elsewhere [12–15] but also summarized in Supplementary Information. The total surface energy as well as its different components (dispersive and acid-base) were determined depending on surface coverage. In the iGC experiments, the normalized surface coverage, n/nm, was calculated as a ratio of number of moles of injected vapor, n, to the number of moles corresponding to a monolayer of coverage for the specific surface area, nm.

A Netzsch STA 449 F3 Jupiter (NETZSCH-Gerätebau GmbH, Selb, Germany) was used for thermal gravimetric analysis (TGA). Calcium oxalate was used for calibration and was within 1% of standard reference values. In an experiment, a controlled environment of 20% argon and 80% oxygen within the instrument chamber was created and a powder sample of 6 mg was placed in an alumina pan. A hole in the center of the pan's lid allowed oxygen from the environment to diffuse into the powder thereby contributing to Al oxidation. Lidded TGA crucibles produce less noise in the signal and provide a more sensitive analysis of mass change. At the beginning of each experiment, the sample was kept for 30 min at room temperature (30 °C) in order to stabilize the instrument. The temperature cycle was designed for both heating and cooling. The target set temperature varied from 600 °C to 640 °C, and the temperature scan rate changed from 5 K/min to 20 K/ min. The value of highest set temperature (640 °C) was chosen to avoid Al melting, so powders preserve morphology. The range of the scan rates was based on preliminary tests that determined regimes to isolate variations in mass change rate. The measured sample mass gain was differentiated to obtain a relative powder reactivity at a given temperature. The difference in the calculated derivative values at heating and cooling at the same temperature (i.e., the reactivity drop) was further analyzed. For this analysis, the normalized reactivity drop, i.e., the difference in derivative values normalized with respect to the derivative value at heating, was calculated at varied temperatures. Data indicating a greater reactivity drop is associated with powder exhibiting greater reactivity thereby producing a thicker aluminum oxide film. Conversely, a lower reactivity drop is associated with less reactive powder and a thinner oxide film.

### 3. Results and discussion

Results of iGC measurements are presented in Fig. 1 for the combined total surface energy and its dispersive and acid-base components. The major result of these measurements is a noticeably lower surface energy of SQ Al compared to UN Al. We believe that the experimentally found difference between surface energies is related to thermal processing of Al particles. A possible mechanism of the surface energy alteration is based on the change in the metal microstructure, and, in particular, on void shrinkage, as described by Zhang et al. [16]. That void shrinkage can also result in the elevated stress in SQ Al that is absent in UN Al [8].



Fig. 1. Surface energy of Al powders. Total energy and its dispersive and acid-base components are obtained depending on surface coverage as defined in the text.

A further study is required to advance that understanding.

The total mass gain in the TGA cycles (heating followed by cooling) varied within the range between 1% and 3.5% depending on the target set temperatures and scan rates. The TGA curves can be characterized by an asymmetry parameter,  $\varepsilon$ , which is defined as

$$\varepsilon \equiv \frac{\Delta m_c}{\Delta m_h} \tag{1}$$

with  $\Delta m_h$  and  $\Delta m_c$  being mass gains during heating and cooling, respectively. Table 1 presents asymmetry parameters calculated according to Eq. (1).

A significant asymmetry of TGA curves, i.e., the parameter  $\varepsilon$  being noticeably smaller than unity, means that the mass gain during heating is measurably greater than that during cooling. As one can see, the revealed asymmetry of TGA curves is more pronounced for UN Al compared to SQ Al. Considering the mass gain is a measure of material oxidation, the effective oxidation rate during cooling is reduced compared to heating, and that reduction is stronger for UN Al (Table 1).

The mass gain derivative of the TGA curve, which is a measure of the oxidation rate, can be utilized in order to further detail the phenomenon. Fig. 2 demonstrates the mass gain derivatives for TGA scans with the target set temperature of 600 °C. A significant derivative drop seen for sample cooling compared to sample heating directly indicates a decrease in the oxidation rate. Decreased oxidation rate can occur due to oxide accumulation on the powder surface during the temperature cycle that reduces oxygen transport toward metal. A comparison of UN Al scans performed at different scan rates allows for the conclusion that this drop is not a hysteresis-like artifact but instead is indeed due to oxidation at select temperatures.

In order to quantify the derivative drop, a normalized derivative drop,  $\eta,$  defined as

$$\eta \equiv \frac{\Delta R}{R} \tag{2}$$

can be used. As illustrated in Fig. 3, the derivative value at cooling is subtracted from the derivative value at heating in order to obtain a difference,  $\Delta R$ . The derivative value at heating, *R*, is used for normalization. Since the normalized derivative drop can be obtained at any temperature, it is a direct characteristics of the oxidation rate reduction

 Table 1

 Asymmetry parameters of the TGA curves at different target set temperatures and scan rates.

	600 °C @ 5 K/ min	600 °C @ 10 K/ min	640 °C @ 10 K/ min	640 °C @ 20 K/ min
SQ A1	0.72	0.87	0.27	0.22
UN Al	0.29	0.61	0.14	0.10



**Fig. 2.** The mass gain derivatives for TGA scans with the target set temperature of 600  $^{\circ}$ C. The arrow shows the temporal scan direction. A comparison of two different scan rates presented for UN Al demonstrates the stronger oxidation drop at the lower scan rate. It allows for the conclusion that the difference between oxidation rates at cooling compared to heating is not a hysteresis-like artifact. A comparison of scans for UN Al and SQ Al at the same scan rate demonstrates a difference between these material behaviors.



**Fig. 3.** Data processing sketch that illustrates how parameters entering calculations of the normalized derivative drop, ie.,  $\Delta R$  and R, can be obtained from the TGA mass gain derivative.

unlike the asymmetry parameter being an integral value. Moreover, at any given temperature,  $\eta$  is calculated using values ( $\Delta R$  and R) obtained at the same temperature, i.e., those corresponding to the same phase of the accumulated alumina film. Then, the normalized derivative drop is a direct indication of oxide accumulation during the temperature scan, with a larger derivative drop indicating stronger oxidation. Thus, a benefit of using the normalized derivative drop is related to the possibility of excluding an alumina phase change, which may occur [17] during temperature scans from the analysis.

Fig. 4 demonstrates the normalized derivative drop of UN Al at two different target set temperatures performed at the same scan rate of 10 K/min. The much bigger drop occurs at the larger target scan temperature, i.e., when the sample was exposed to higher temperatures and more oxide accumulation inherently occurs. Fig. 4 shows that oxide accumulation is a strong function of temperature, and higher oxidation temperatures will produce thicker films.

A comparison of normalized derivative drops for UN Al and SQ Al (see Fig. 5) clearly shows that the UN Al drop is consistently higher compared to the SQ Al drop.

Two major conclusions about the normalized derivative drop behavior can be drawn based on the analysis of the results presented above:

- Powder exposure to an oxygen environment at higher temperatures leads to a more pronounced drop for both powders studied.
- At the same exposure to higher temperatures, the drop for UN Al is noticeably bigger compared to SQ Al.

The only reasonable explanation for the derivative drop is an oxide accumulation on the surface of metal particles during the thermal experiment. A thicker oxide leads to a relatively lower oxidation rate at cooling compared to heating. Then, a bigger drop for UN Al compared to SQ Al means a larger amount of oxide accumulated on the UN Al powder surface during the same temperature cycle. The latter can only be possible if the initial rate of UN Al oxidation is higher compared to SQ Al and that means a higher initial reactivity of UN Al powder.

The conclusion on the different oxide accumulation for UN Al compared with SQ Al drawn from the analysis of Fig. 5 is more reliable than what could be obtained from the transmission electron microscope (TEM) diagnostics. Based on the total mass gain observed in the TGA experiments, the thickness of accumulated oxide shells is on the order of 10 nm. Assuming that the difference between UN Al and SQ Al is on the order of 10%, the TEM analysis should statistically distinguish a



Fig. 4. Normalized derivative drop for the 10 K/min scans with UN Al performed at two different target set temperatures.

thickness difference of about 1 nm that could be doable, in principle. The major issue is, however, related to the sample recovery from the TGA instrument. It will essentially involve an additional powder oxidation during cooling that is stronger for SQ Al (see Fig. 2). Thus, the powder samples available for the TEM would be compromised leading to an inaccurate interpretation. On the contrary, the normalized derivative drop analysis, which deals with in situ data, is free of those TEM issues.

It should be noted that the discussed reactivity is a characteristic of powders and is not dependent on the powder heating rates. Then, the higher reactivity of UN Al powder at low temperatures extends to significantly higher heating rates relevant to combustion conditions.

It is worth noting that the revealed link between surface energy and reactivity of Al particles likely originates from the Arrhenius-like behavior of metal oxidation [18]. Surface energy can influence oxygen adhesion affecting the molecule residence time on the surface, and, therefore, the magnitude of the pre-exponent. An initial energetic state of oxygen migrating across the shell is also dependent on the surface energy, which can affect the activation barrier as well. These phenomena are worth further studies.

The different low temperature reactivity of super-quenched and untreated aluminum particles demonstrated in the current work allows for filling gaps in understanding of their distinctive combustion behaviors. As shown in Fig. 6, the thermal processing leads to elevated stress and a lower surface energy. Results from this study show surface energy governs pre-ignition oxidation resulting in a thinner oxide film for SQ Al. Thus, SQ Al burns more intensively compared with UN Al, because a thinner oxide barrier reduces diffusion times that result in faster burning Al particles. The insights gained from the experiments designed here explain a mechanism responsible for differences in burn time. Explicitly, the mechanism is variation in oxide film formation thickness resulting from particle surface energy differences.

### 4. Concluding remarks

The TGA study performed in the current paper provides evidence of higher initial reactivity of UN Al compared to SQ Al at low temperatures (i.e., < 640 °C). A unique data analysis approach is introduced to tweeze out the development of an oxide film associated with particle interface reactions. It is worth emphasizing that the reactivity characterization methodology, which is based on the normalized derivative drop analysis, developed in the current paper may be of general interest as a novel analytical tool.

Being linked to the measured particle surface energy, low temperature Al oxidation is concluded to increase with that surface energy. The stronger reactivity of UN Al at low temperatures leads to more oxide accumulation (i.e., a thicker oxide film) on the metal particle surface during their pre-ignition heating. Thus, UN Al ignites with a surface oxide film that is thicker compared to SQ Al. The development of an oxide film and its distinct variation in thickness with surface energy is a possible explanation of the mechanism of different modes of aluminum combustion depending on the particle thermal treatment. On the other hand, the correlation between the particle surface energy and reactivity at low temperatures established in the current work can guide further development of metal fuels for different applications, in which either slow or fast combustion is beneficial.

#### Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

# CRediT authorship contribution statement

Islam Shancita: Investigation. Igor Altman: Conceptualization, Methodology, Formal analysis, Writing – original draft. Daniel Burnett: Investigation, Writing – original draft. Ezequiel Gutierrez Zorrilla:



Fig. 5. Normalized derivative drop for the different scan rates performed at the target set temperature of (a) 600 °C and (b) 640 °C.



Fig. 6. Concept sketch summarizing the thermal processing effect on the combustion behaviors of aluminum particles. Thermal processing leads to elevated stress and lower surface energy. Surface energy influences pre-ignition oxidation resulting in a thinner oxide film for SQ Al. Thus, SQ Al burns with more intensity compared with UN Al.

Investigation. Armando R. Garcia: Investigation. Kevin Hill: Formal analysis. Michelle Pantoya: Supervision, Visualization, Writing – review & editing, Funding acquisition, Project administration.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

The U. S. Office of Naval Research (N00014–22–1–2006) and our program manager, Dr. Chad Stoltz are gratefully acknowledged. The authors are thankful for partial support from ONR STEM grant N00014–21–1–2519. I.A. is also thankful for funding from the NAVAIR ILIR program managed at the ONR and administered by Alan Van Nevel.

# Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.tca.2023.179521.

# References

- K. Brooks, M. Beckstead, Dynamics of Aluminum Combustion, J. Propuls. Power 11 (1995) 769–780, https://doi.org/10.2514/3.23902.
- [2] M. Beckstead, Y. Liang, K. Pudduppakkam, Numerical simulation of single aluminum particle combustion (Review), Combust. Explos. Shock Waves 41 (2005) 622–628, https://doi.org/10.1007/s10573-005-0077-0.
- [3] D. Sundaram, P. Puri, V. Yang, A general theory of ignition and combustion of nano- and micron-sized aluminum particles, Combust. Flame 169 (2016) 94–109, https://doi.org/10.1016/j.combustflame.2016.04.005.
- [4] D. Sundaram, V. Yang, R.A. Yetter, Metal-based nanoenergetic materials: synthesis, properties, and applications, Prog. Energy Combust. Sci. 61 (2017) 293–365, https://doi.org/10.1016/j.pecs.2017.02.002.
- [5] I. Altman, A. Demko, K. Hill, M. Pantoya, On the possible coexistence of two different regimes of metal particle combustion, Combust. Flame 221 (2020) 416–419, https://doi.org/10.1016/j.combustflame.2020.08.015.

- [6] Q. Tran, M.L. Pantoya, I. Altman, Condense-luminescence and global characterization of metal particle suspension combustion, Appl. Energy Combust. Sci. 11 (2022), 100080, https://doi.org/10.1016/j.jaecs.2022.100080.
- [7] I. Altman, M. Pantoya, Comprehending metal particle combustion: a path forward, Propellants Explos. Pyrotech. 47 (2022), e202200040, https://doi.org/10.1002/ prep.202200040.
- [8] K. Hill, N. Tamura, V. Levitas, M. Pantoya, Impact ignition and combustion of micron-scale aluminum particles pre-stressed with different quenching rates, J. Appl. Phys. 124 (2018), 115903, https://doi.org/10.1063/1.5044546.
- [9] K. Hill, M. Pantoya, E. Washburn, J. Kalman, Single particle combustion of prestressed aluminum, Materials 12 (2019) 1737, https://doi.org/10.3390/ ma12111737.
- [10] A. Williams, I. Shancita, N. Vaz, T. Tran-Ngo, A.A.I. Demko, I. Altman, K. Hill, D. Tunega, A. Aquino, M. Pantoya, Stress-altered aluminum powder dust combustion, J. Appl. Phys. 127 (2020), 175110, https://doi.org/10.1063/ 5.0002737.
- [11] A. Williams, I. Shancita, I. Altman, N. Tamura, M. Pantoya, On the pressure generated by thermite reactions using stress-altered aluminum particles, Propellants Explos. Pyrotech. 46 (2021) 99–106, https://doi.org/10.1002/ prep.202000221.

- [12] J.B. Donnet, S.J. Park, H. Balard, Evaluation of specific interactions of solid surfaces by inverse gas chromatography: a new approach based on polarizability of the probes, Chromatographia 31 (1991) 434–440, https://doi.org/10.1007/ BF02262385.
- [13] G.M. Dorris, D.G. Gray, Adsorption of n-alkanes at zero surface coverage on cellulose paper and wood fibers, J. Colloid Interface Sci. 77 (1980) 353–362, https://doi.org/10.1016/0021-9797(80)90304-5.
- [14] C.J. van Oss, Interfacial Forces in Aqueous Media, Marcel Dekker, New York, 1994.
- [15] K.L. Mittal, Contact Angle, Wettability and Adhesion v3, Utrecht, Boston, 2003.
- [16] Z. Zhang, T. Liu, A.E. Smith, N.V. Medhekar, P.N.H. Nakashima, L. Bourgeois, Mechanisms of void shrinkage in aluminium, J. Appl. Crystallogr. 49 (2016) 1459–1470, https://doi.org/10.1107/S1600576716010657.
- [17] J. Gao, J. Yan, B. Zhao, Z. Zhang, Q. Yu, In situ observation of temperaturedependent atomistic and mesoscale oxidation mechanisms of aluminum nanoparticles, Nano Res. 13 (2020) 183–187, https://doi.org/10.1007/s12274-019-2593-3.
- [18] A.B. Vorozhtsov, M. Lerner, N. Rodkevich, H. Nie, A. Abraham, M. Schoenitz, E. L. Dreizin, Oxidation of nano-sized aluminum powders, Thermochim Acta 636 (2016) 48–56, https://doi.org/10.1016/j.tca.2016.05.003.