

Projektnummer/Project no Uppdragsgivare/Client  
E20919 Försvarsmakten  
FoT-område  
Vapen och skyddFörfattare/Author  
Niklas ZettervallDatum/Date  
2022-12-12Memo nummer/Number  
FOI Memo 7993

# 1 Mot förbättrad förståelse för aluminiumförbränning

## 1.1 Inledning

Aluminium har använts som tillsats i spräng- och drivladdningar i årtionden. Aluminium har fördelen att mycket energi frigörs vid dess förbränning, vilket ökar laddningarnas verkan och räckvidd. Trots detta är dagens modeller för aluminiumförbränning otillräckliga för beräkning av prestanda. Detta innebär att dessa modeller inte kan användas för att beräkna prestanda hos en spräng- eller drivladdning med en annan utformning eller funktion, än vad de utvecklades för.

I en detonation, som är en mycket snabb process med väldigt hög temperatur, reagerar (i reaktionszonen) aluminium inte under själva detonationen, utan med de gaser som då bildas. Detta brukar benämnas efterförbränning och denna varar i en tidsrymd av storleksordningen millisekunder. Temperaturen uppgår till tusentals grader.

I en drivladdning sker förbränningen långsammare och vid lägre temperatur. Vanliga temperaturer är dock ändå bortåt 2500 °C eller högre, och förbränningszonen flyttar sig några millimeter per sekund.

De stora skillnaderna i temperatur, tryck och reaktionstid gör att det är svårt att utveckla en modell som fungerar för alla temperaturer och tidsrymder. Därför används i dag många olika modeller för olika tillämpningar.

Modellerna är viktiga för att prestandan hos nya vapensystem ska kunna optimeras. De kan också användas för teknisk underrättelse, t.ex. beräkningar av räckvidden hos motståndarens robot, då en sådan eller dess ritningar hittats.

FOI har därför gjort en litteraturstudie, som sammanfattas och presenteras i detta memo. En kortare sammanfattning av litteraturstudien, på svenska, följer nedan, och sedan följer litteraturstudien på engelska som sista del i detta dokument. Litteraturstudien har skrivits på engelska, så att den ska kunna användas i internationella samarbeten.

## 1.2 Sammanfattning av litteraturstudien

Då aluminium är en nyckelkomponent i många tillämpningar, både för detonations- och deflagrationsförlopp, utgör möjligheter till dess modellering en central del i den kapacitet och kunskap FOI bör besitta. Med detta sagt är modelleringen av aluminium, oavsett tillämpning, en mycket komplicerad uppgift och någon som kräver en bred bas av kunskaper inom flera olika områden. Simuleringar av aluminium innebär komplexa interagerande fysikaliska delar såsom fasövergångar (fast → vätska → gas), yt- och gasformiga reaktioner, inhomogen temperaturfördelning hos partiklarna, komplex reaktionskinetik för att beskriva det reaktiva förloppet, partikeldynamik, strömningsdynamik o.s.v.

Titel/Title  
Mot förbättrad förståelse för aluminiumförbränning

Memo nummer/Number  
FOI Memo 7993

För att kunna modellera aluminiumförbränning på ett adekvat sätt kommer man, oavsett tillämpning, med största sannolikhet behöva kunna modellera förbränningsförloppet hos en enskild partikel. Under de senaste åren har den detaljerade kunskapen om hur en aluminiumpartikel oxiderar under förbränning vuxit och kan kortfattat beskrivas enligt följande:

1. Steg I, där aluminiumpartikeln hettas upp och dess yta börjar koka (fasövergång, fast → vätska). Denna vätska har delvis förångats och partikeln omges av gasformig aluminium. I utkanten av detta moln med aluminium sker reaktioner med omgivande gas (tex vatten, luft, reaktionsprodukter från explosivämne), resulterandes i en diffusionsflamma.
2. I Steg II har molnet med aluminiumgas runt partikeln minskat något och en del av slutprodukterna av förbränningen av det omgivande målet, aluminiumoxid, kommer att fastna på partikelns yta och bilda ett kemiskt stabilt oxidlager som i sin tur försvårar ytterligare reaktioner och som gör ytan okänslig för omgivningen.
3. Slutligen i Steg III fortsätter molnet av aluminiumgas runt partikeln minska. Den ursprungliga partikeln har minskat avsevärt i storlek medan det fästa oxidlagret har vuxit och är i detta skede större än den kvarvarande aluminiumpartikeln.

FOI:s bedömning är att en början till modellering av det förlopp som beskrivs ovan kommer vara centralt för framtida, större och mer tillämpningsnära, simuleringar. När man väl kan hantera en modellering av ovan nämnda uppställning, kan man börja göra eventuella förenklingar eller ytterligare modelleringsarbeten med syfte att kunna ta den övergripande modelleringen till mer storskaliga tillämpningar. När en grundförståelse för hur aluminium oxiderar och fysiken bakom detta förlopp finns, kommer det med största sannolikhet att vara möjligt att kunna tillämpa modelleringen på olika fall. Till exempel, kommer byte av omgivande oxidator, främst luft eller olika kompositioner av förbränningsprodukter från explosivämnen, vara ett enkelt skifte att göra, likaså för olika tryck och temperaturer som aluminiumet kommer stöta på beroende på applikation där det används.

I den initiala genomgång, har fokus legat på att skaffa en överblick hur man kan välja att ta sig an dessa modelleringsproblem. Med detta sagt, har arbete som undersöker tillgänglig kemisk kinetik för aluminiumförbränning redan påbörjats. FOI har också tittat på kvalitén hos olika i litteraturen tillgängliga termodynamiska data.

Titel/Title  
Mot förbättrad förståelse för aluminiumförbränning

Memo nummer/Number  
FOI Memo 7993

## 2 Literature study

### 2.1 Towards modelling of aluminium combustion

Aluminium combustion is a key component in many applications, both in deflagration and detonation regimes. It is often used as an additive in solid propellants and explosives thanks to its good energy characteristics, and its possibility to extend the pressure curve. Aluminium can be considered as a (metal) fuel, but one with higher melting and boiling points than fossil fuels.

The combustion process of aluminium particles is highly complex, including both high temperatures, gas and surface reactions, nonlinear temperature profiles inside particles, boiling and evaporation of aluminium particles and the formation of an oxide cap on the particle surface (1). The adiabatic flame temperature for aluminium combustion is greater than the boiling point of aluminium. For an aluminium particle burning in oxygen for example, the boiling point is 2791 K, whereas the flame temperature is around 4000 K. Higher pressures can delay the boiling point to occur at even higher temperatures. The feedback of heat from the flame surrounding the particle vaporizes the particle surface and the vapour proceeds to burn homogeneously (2). One exception to this is when aluminium particles burn in CO gas, where they burn heterogeneously.

In the combustion process, the temperature of the particle is constantly changing, and an initially small oxide cap will form and start to grow. This can change the centre of mass of the particle, which can then rotate and micro-explode (1). Some of the oxidizers will penetrate through the vapour phase and reach the liquid surface of the boiling aluminium particle, where surface reactions will occur.

The combustion of aluminium can be divided into three stages:

- Stage I is where the aluminium particle is heated and starts to boil, and the particle is surrounded by aluminium vapour. At the outer edge of the aluminium vapour, the vapour meets the surrounding oxidizer, resulting in a diffusion flame.
- In Stage II, the aluminium vapour decreases somewhat, the particle continues to evaporate and a small oxide cap will form on the surface of the particle.
- In Stage III, the original particle has almost completely vaporized, the aluminium vapour is even smaller than in the previous two stages and the oxide cap has started to grow and constitutes the majority of the particle that is left.

Important features to capture in any modelling effort is the chemical kinetics of both gas phase and surface reactions, heat conduction, transport of species in and out of the gaseous aluminium layer as well as radiation from the burning gaseous phase heating the particle.

#### 2.1.1 Chemical kinetics

The chemical kinetic modelling plays a key role when simulating aluminium combustion, both in the gas phase and for the surface reactions of the aluminium particle. Kinetics for both gas phase and for surface reactions are described below.

When the gas phase aluminium burns with the surrounding oxidizer(s), the aluminium sub-oxides – such as  $\text{AlO}$  and  $\text{AlO}_2$  – are key intermediate species in the kinetics of the aluminium combustion. Experiments have shown that these intermediates are present close to the particle surface (2). These intermediate sub-oxides will condense to form liquid aluminium oxide,  $\text{Al}_2\text{O}_3$  (2). The major product of the aluminium combustion, the liquid  $\text{Al}_2\text{O}_3$ , will have a small fraction that will diffuse back and deposit onto the particle surface, forming the so called oxide cap (2). This oxide cap can in later stages of the combustion be greater in size than the (shrinking) particle itself. However, the majority of the  $\text{Al}_2\text{O}_3$  formed will be transported outwards and is often termed *oxide smoke*, and can be seen as white trails of smoke.

Titel/Title

Mot förbättrad förståelse för aluminiumförbränning

Memo nummer/Number

FOI Memo 7993

Thermodynamically, the heat of reaction in the formation of  $\text{Al}_2\text{O}_3$  from sub-oxides is sufficient to cause the dissociation of the newly formed  $\text{Al}_2\text{O}_3$ . This means that the sub-oxides reaction pathway [sub-oxides  $\rightarrow \text{Al}_2\text{O}_3(\text{l})$ ] cannot occur. Instead, there is most probably (according to the mechanism by Glorian (3), see below) a set of reactions where  $\text{Al}_2\text{O}_3$  forms in other, gaseous states, which then can condense (2). In that reaction mechanism, sub-oxides, such as  $\text{AlO}$ ,  $\text{AlO}_2$  and  $\text{Al}_2\text{O}_2$ , form  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3(\text{c})$ , which then condenses into  $\text{Al}_2\text{O}_3(\text{l})$  in a later step. A similar approach was suggested by Beckstead (2) as well.

Bucher *et al.* (4) measured the temperature distribution of the ambient air and the gas phase composition during the combustion and suggests that the peak in  $\text{AlO}$  concentration best represents the position of the flame. When one investigates the chemical kinetics of aluminium combustion, it becomes clear the  $\text{AlO}$  plays a central role, being a key intermediate species in the combustion.

### 2.1.2 Gaseous phase

Several chemical kinetic reaction mechanisms for gas phase exists. Washburn *et al.* (5) developed a gas phase kinetic mechanism for the  $\text{Al/Cl/O/C/H}$  system and applied to simulation of micro-sized particles. Later versions of that mechanism was extended to also include simulations with steam and carbon dioxide (6). It totalled 33 species and 89 reactions.

The PhD work by Glorian *et al.* (3) presented an  $\text{Al/C/H/O}$  mechanism, later used in by Hu *et al.* (1). The aluminium reactions are coupled to a set of  $\text{H}_2\text{-O}_2$  reactions as well as  $\text{CO/CO}_2$  reactions and a submechanism for  $\text{Cl}$  reactions both with  $\text{Al}$  and  $\text{H}_2\text{-O}_2$ . There are however some possible limitations of the mechanism. First of all no  $\text{NO}_x$  chemistry is included, itself not an issue if  $\text{N}$  and  $\text{O}$  is not present in an oxidizer, but a potential limitation if they are. The reason for this is that the highly temperature-dependent  $\text{NO}_x$  formation will both affect (lowering) the temperature of the mixture, effectively decreasing the rate of reaction, and affect the production of  $\text{O}$  atoms, a key component in the formation of  $\text{AlO}$ , a precursor for both  $\text{OAlO}$  and  $\text{AlOAlO}$ . The two latter species are precursors for both  $\text{AlOAlO}$  and  $\text{Al}_2\text{O}_3$  in the mechanism.

Another limitation of the mechanism is the poor predictability of the ignition delay time for a  $\text{H}_2\text{-O}_2$  mixture. To illustrate the performance issue the ignition delay time for  $\text{H}_2\text{-O}_2$  mixtures at stoichiometric conditions, at 4 and 16 atm, are shown in Fig. 1 below. Even though the mechanism itself is not designed for pure  $\text{H}_2\text{-air}$  conditions, the fact that the predictability of the underlying  $\text{H}_2\text{-O}_2$  mechanism is so poor raises questions if that mechanism can at all be used as a base for the  $\text{Al}$ -chemistry. The plots in Fig. 1 shows that it is only the Z24 mechanism that is capable of predicting the ignition delay times over a wide range of temperatures.

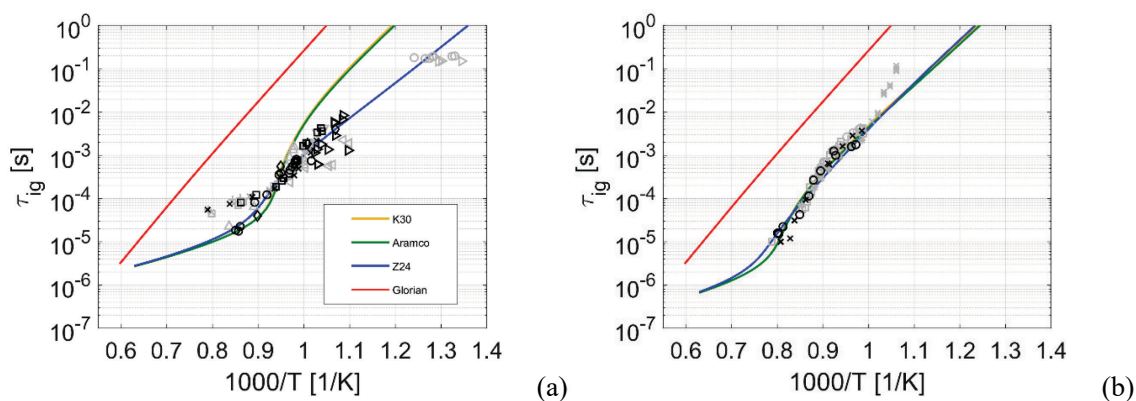


Fig. 1. Ignition delay times at stoichiometric conditions, at 4 atm in (a) and 16 atm in (b). Black symbols represents experimental data at stoichiometric conditions and grey symbols at other equivalence ratios.

Titel/Title

Mot förbättrad förståelse för aluminiumförbränning

Memo nummer/Number

FOI Memo 7993

All of these issues aside, the underlying Al sub-mechanism can be extracted and used together with another H<sub>2</sub>-O<sub>2</sub> sub-mechanism, but with the correction that both reactions forming liquid Al<sub>2</sub>O<sub>3</sub> becomes reversible, as suggested by Hu *et al.* (1). This is due to the fact that even though the liquefaction of aluminium at high-temperatures is fast, the combustion temperature of almost 4000 K in air means that the reverse reaction cannot be ignored.

A suitable H<sub>2</sub>-O<sub>2</sub> reaction mechanism to use as a base, together with a detailed NO<sub>x</sub> mechanism, is possibly the recent NUI 1.1 mechanism (7) (a continuation of the Aramco mechanism in the figures above), originally designed for C<sub>1</sub>-C<sub>7</sub> alkanes but that also includes a very detailed set of H<sub>2</sub>-O<sub>2</sub> and NO<sub>x</sub> reactions. Coupling this mechanism, with its NO<sub>x</sub> sub-mechanism, to the aluminium mechanism by Glorian *et al.* (3) creates a solid mechanism that can be used for aluminium gas phase simulations in either air, detonation products (CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O) and in pure water vapour. Another option is to couple the aluminium mechanism to the Z24 mechanism with a simplified NO<sub>x</sub> sub-mechanism attached. This option presents a smaller mechanism, i.e. with a lower computational cost which is important in 3D computational fluid dynamic (CFD) simulations, and one which can handle the ignition delay time in the lower pressure regions (1-8 atm).

### 2.1.3 Surface reactions

For species in surface formalism, there are three types: i. gas phase, ii. surface and iii. bulk. The first species, in gas phase, (i.) is a species above the particle surface, denoted just Al. Reactions present at the particle surface (ii.) is denoted by (S), and the open at the surface of the particle is denoted by Al(L). Finally, in the bulk regime (iii.) the liquid aluminium is denoted by Al(B). When it comes to surface site species the most important ones are Al(L), Al<sub>2</sub>O(S) and Al<sub>2</sub>O<sub>2</sub>(S) (1). Surface reactions are expected to be slower than gas phase reactions (2). Also, it has been observed that the aluminium sub-oxides do not dissolve in the metal but rather stay on the surface (2).

As for the gas phase the work by Glorian *et al.* (3) provides a detailed mechanism for the surface chemistry. When modelling the surface reactions the general rate-of-progress variable combines the gas and surface reactions, and surface molar concentrations is separately calculated, as described by Dreizin *et al.* (8).

### 2.1.4 Thermodynamic data

Before simulating any combustion case thermodynamic data needs to be found and collected. Here data in the NASA 7-polynomial format has been collected, taken from either Goos *et al.* (9), or directly from the mechanism of Glorian (3). These polynomial constants are used to calculate molar heat capacity at constant pressure, C<sub>p</sub><sup>0</sup>(T), the molar enthalpy, h(T<sub>0</sub>, p<sub>0</sub>), and the absolute molar entropy, s(T<sub>0</sub>, p<sub>0</sub>), at reference temperatures and pressures, T<sub>0</sub> and p<sub>0</sub>, respectively.

Species data for Al, AlO, AlOAlO, AlOAl, OAlO, Al<sub>2</sub>O<sub>3</sub>, AlH<sub>3</sub>, AlH<sub>2</sub>, AlH, Al<sub>2</sub>O<sub>3</sub>(l), Al<sub>2</sub>O<sub>3</sub>(a) and Al<sub>2</sub>O<sub>3</sub>(b) have been sampled. For the data from Goos *et al.* (9), the gaseous species Al, AlO, AlOAlO, AlOAl, OAlO, Al<sub>2</sub>O<sub>3</sub>, AlH<sub>3</sub>, AlH<sub>2</sub> and AlH all have temperature ranges of 200 K to 1000 K, and then 1000 K to 6000 K. Al<sub>2</sub>O<sub>3</sub>(l) has a range from 2327 K to 6000 K, Al<sub>2</sub>O<sub>3</sub>(b) from 1200 K to 2327 K and finally Al<sub>2</sub>O<sub>3</sub>(a) from 200 K to 700 K and then from 700 K to 1200 K. For the data of Glorian (3) the temperature ranges used varies, but are generally from 300 K up to between 4000 and 5000 K. Note also that the species AlH<sub>3</sub>, AlH<sub>2</sub> both tops out at 1500 K, making it questionable if these data sets can be used.

To demonstrate the different data resulting from the different Al<sub>2</sub>O<sub>3</sub> species and their respective temperature ranges the heat capacity and the enthalpy has been plotted for Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>(l), Al<sub>2</sub>O<sub>3</sub>(a) and Al<sub>2</sub>O<sub>3</sub>(b), for the Goos data, and Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>(L), Al<sub>2</sub>O<sub>3</sub>(c) for the Glorian data. All data is shown in Fig. 2. Al<sub>2</sub>O<sub>3</sub>(a) and Al<sub>2</sub>O<sub>3</sub>(b) corresponds to aluminium at the center and surface of the particle, respectively. Here it is clear that the data from Al<sub>2</sub>O<sub>3</sub>(a) connects to that of Al<sub>2</sub>O<sub>3</sub>(b), and that there is a jump where the data for Al<sub>2</sub>O<sub>3</sub>(b) ends and Al<sub>2</sub>O<sub>3</sub>(l) starts. This jump is equivalent to the enthalpy

Titel/Title  
Mot förbättrad förståelse för aluminiumförbränning

Memo nummer/Number  
FOI Memo 7993

change due to the phase shift at these temperatures. The gaseous version of  $\text{Al}_2\text{O}_3$  has a continuous curve for the complete temperature range.

The Glorian data show completely different curves than the Goos data. First of all, the  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3(\text{c})$  both uses the same thermodynamic data (green dotted on top of red dashed lines). Also, the Glorian data show very different behaviour for  $C_p$ , without a jump. The data for  $H^0$  is in line with the Goos data. It is also interesting to note that the Glorian data ends at 4000 K, even though the temperature in aluminium combustion can be in excess of that.

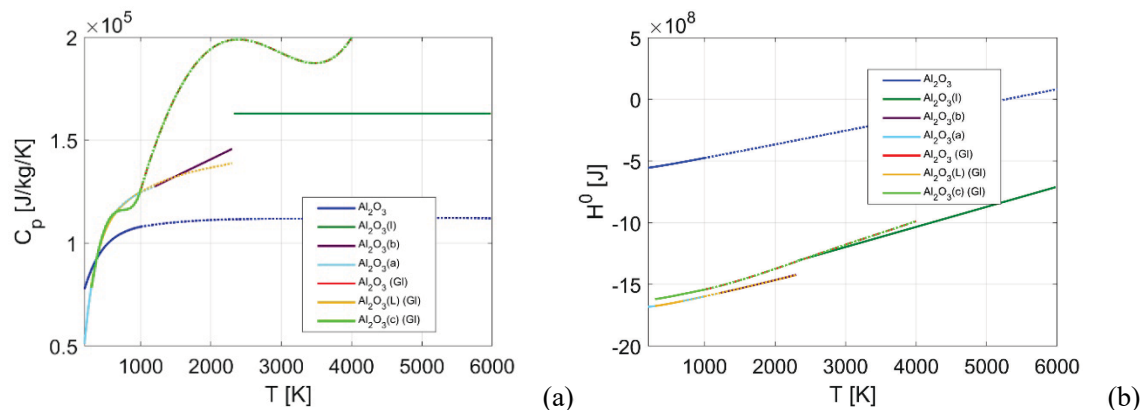


Fig. 2. Thermodynamic data,  $C_p$  (a) and  $H^0$  (b), plotted for different states of the  $\text{Al}_2\text{O}_3$  species. Note the jump in data for where an enthalpy change occurs during phase shifts of the species.

### 2.1.5 Particle temperature modelling

The melting temperature of the aluminium cannot always be considered constant, hence, the temperature profile inside aluminium particle cannot be considered homogeneous for all sizes of particles, and therefore needs to be modelled. Ideally this needs to be made in as computationally cheap way as possible, and the work by Baudin *et al.* (10) provides one simple modelling approach. Two modelling approaches presented in that study uses one approach called “the simplified model”, with enough accuracy and a desirably low computational cost. It therefore represent a suitable choice of model for inclusion into three dimensional CFD codes.

## 2.2 References

1. Hu, Z., Yang, T., Xia, Z., Ma, L., Li, M., & Feng, Y. The simulation of different combustion stages of micron-sized aluminum particles. *Appl Sci.* 2021;11(4):1774.
2. Beckstead, M. W. A Summary of Aluminium Combustion. Brigham Young Univ Provo Ut.; 2004.
3. Glorian J. Cinétique hétérogène pour la combustion de l'aluminium [Doctoral Dissertation]. [Paris]: ENSTA Paris Tech; 2014.
4. Bucher, P., Yetter, R. A., Dryer, F. L., Parr, T. P., Hanson-Parr, D. M., & Viceni, E. P. Flames structure measurement of single, isolated aluminum particles burning in air. *Symp Int Combust.* 1996;26(2):1899–908.
5. E.B. Washburn, J.N. Trivedi, L. Catoire, M.W. Beckstead. The simulation of the combustion of micrometer-sized aluminum particles with steam. *Combust Sci Technol.* 2008;180:1502–17.
6. E.B. Washburn, J.A. Webb, M.W. Beckstead. The simulation of the combustion of micrometer-sized aluminum particles with oxygen and carbon dioxide. *Combust Flame.* 2010;157:540–5.

Titel/Title

Mot förbättrad förståelse för aluminiumförbränning

Memo nummer/Number

FOI Memo 7993

7. Wu, Y., Panigrahy, S., Sahu, A. B., Bariki, C., Beeckmann, J., Liang, J., ... & Curran, H. J. Understanding the antagonistic effect of methanol as a component in surrogate fuel models: A case study of methanol/n-heptane mixtures. *Combust Flame*. 2021;226:229–42.
8. Dreizin, E.L. Experimental study of stages in aluminium particle combustion in air. *Combust Flame*. 1996;105(4):541–56.
9. Goos, E.; Burcat, A.; Ruscic, B. Extended Third Millenium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with updates from Active Thermochemical Tables. received from Elke Goos, Elke.Goos@dlr.de April 2015. 2015.
10. Baudin, G., Genetier, M., Elia, T., & Catoire, L. Aluminum powder heat and combustion modeling inside the detonation products of high explosives. 16th Int Detonation Symp. 2018;194.