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Influence of passivation on ageing of nano-aluminum: Heat flux calorimetry and microstructural studies

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ABSTRACT

Aluminum nanoparticles (*n*-Al) have been considered as promising fuel for incorporation in propellants and explosives to improve their performance. To prevent oxidation during storage, we investigate the effect of organic coatings on reducing oxidation of *n*-Al via accelerated ageing tests. The *n*-Al was modified with 3 different functional organic silanes. The presence of organic coatings on surface-modified *n*-Al was confirmed by X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). In the accelerated ageing tests, the pristine and surface-modified *n*-Al were kept at elevated humidity and temperatures. The ageing process was monitored via heat flow calorimeter. The effectiveness of the organosilane coatings as barrier to hydrolysis and oxidation of *n*-Al was evaluated from the heat released during ageing, as well as the analysis of active Al content of the aged samples. It is found that although the pristine *n*-Al possesses a natural Al_2O_3 passivation layer, it cannot prevent *n*-Al from fully getting oxidized under the conditions tested. Organosilane coatings act as excellent barrier against diffusion of moisture preventing *n*-Al inside from oxidation. This study shows that all 3 kinds of organosilane-modified *n*-Al have much better resistance to ageing than the pristine *n*-Al, therefore demonstrates surface-modification of *n*-Al is a promising technique to extend the shelf life of *n*-Al during storage.

1. Introduction

Nanometric Aluminium (*n*-Al) has been used as a fuel component in the energetic material formulations because of its high volumetric heat of combustion. As compared to micron scale counterparts, the essential characteristics of *n*-Al that lead to enhanced reactivity are smaller particle size and correspondingly higher surface area to volume ratio. There have been several reports on the enhancements of combustion as a result of the addition of *n*-Al particles to solid propellants and also to energetic nanocomposites. The reported enhancements include improvement in burn rates and shorter ignition delay [1–4].

n-Al powders undergo ageing under humid conditions by the formation of a passive layer of Aluminum hydroxide ($Al(OH)_3$) [5], reducing the overall active Al content. Lower active Al content leads to significant reduction in the volumetric heat of combustion of particles resulting in limited realization of the energy potential of the fuel. Due to the enhanced reactivity, the ageing problem is more severe in *n*-Al particles as compared to the micron Al particles. *n*-Al loses 90% of active Al content under storage at 40 °C and 75% relative humidity for a period of 20days. On the other hand, micron Al loses only 25% of active Al content in the corresponding period under the same conditions [6]. The excessive oxidation of *n*-Al is a significant drawback associated with the usage of *n*-Al in energetic applications. Furthermore, the high surface area of the *n*-Al leads to agglomeration of the particles in the binder resulting in processability problems.

Surface functionalization of aluminum oxide surfaces by suitable modifiers has been demonstrated as a viable method not only for preventing the loss of active Al under ageing but also to improve the dispersion of *n*-Al particles in the binder. Representative modifiers include different type of silanols [7], hydroxamic acids [8], carboxylic acids [9] and hydroxyl terminated polybutadiene (HTPB) polymer [10]. Surface functionalization of oxide free *n*-Al surfaces has also been demonstrated by self-assembly of a monolayer of pefluorinated carboxylic acid [11].

With increasing demand for *n*-Al in energetic materials industry, understanding the energy release during the ageing process of *n*-Al has become very important especially in its storage and for assessment of their fire and explosion safety. The energy release and associated kinetics during the storage of *n*-Al under different conditions of humidity and temperature has not been investigated.

Micro-calorimetry is an ultra-sensitive technique that enables the measurement of very small heat flow (in nano-watt range)

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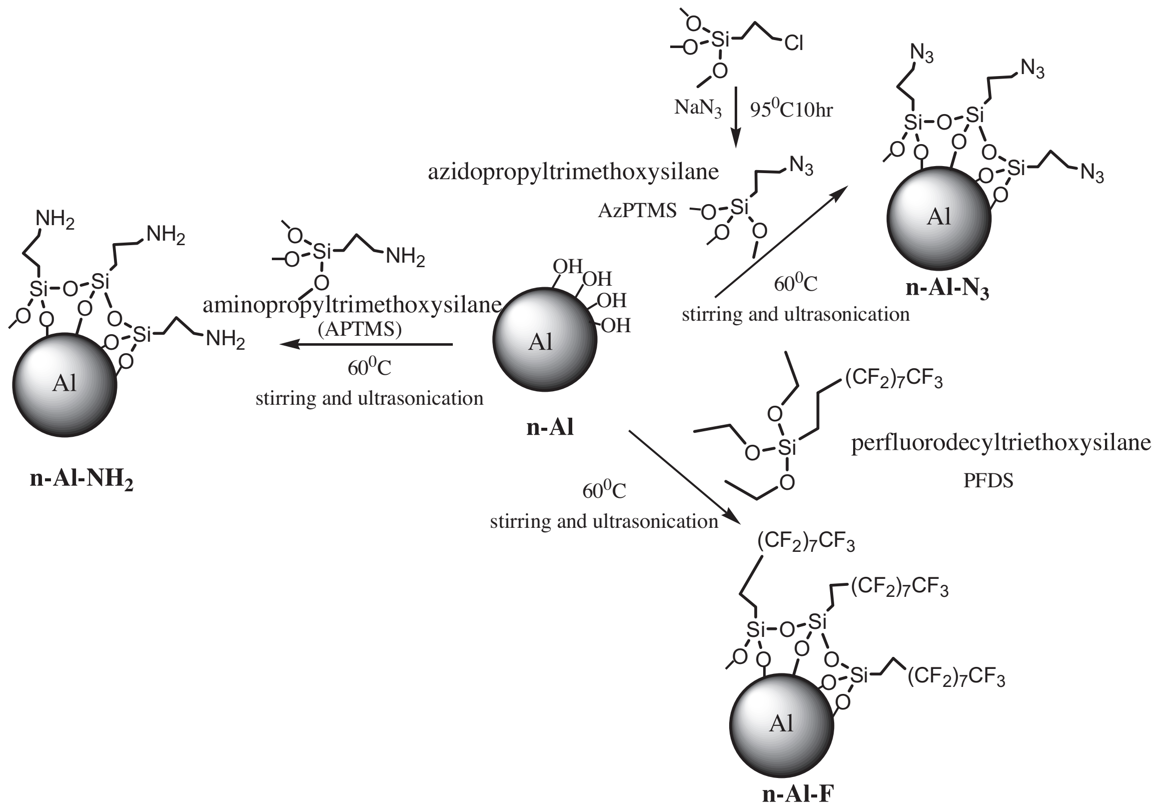
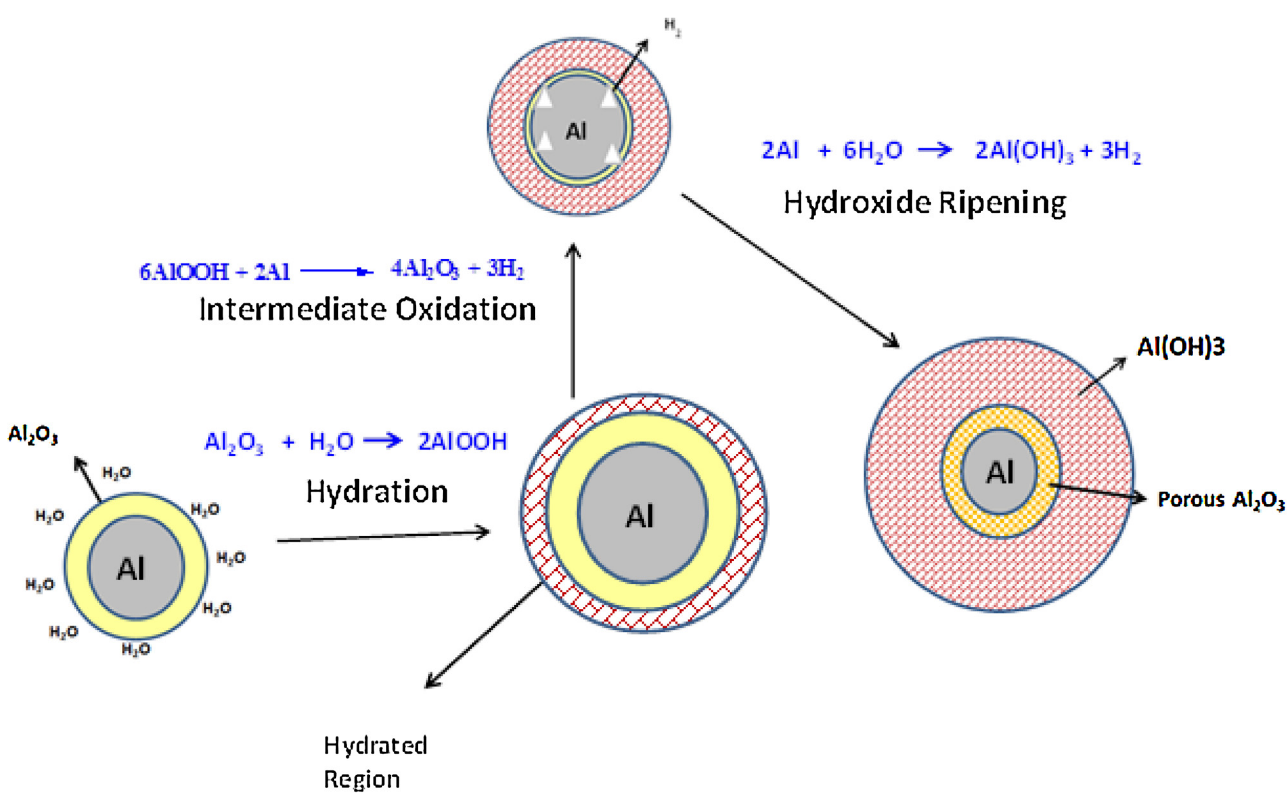


Scheme 1. Reaction scheme for surface modification of *n*-Al using different silanes.



Scheme 2. Reactions involved in the nano-Al hydration process.