Optimising in-situ nitridation in piled aluminium flakes for novel closed cell composites with high fracture stress and toughness

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HIGHLIGHTS

- The highly exothermic nitridation activates melting and penetration of Al through growing cracked AlN shells on the flakes.
- Peak shape dependencies between the structure porosity or AlN volume fraction and the specific toughness are revealed.
- The novel syntactic Al foam with closed pores has a specific strength (toughness) of about 230 MPa cm^3 g^{-1} (50 J g^{-1}).

GRAPHICAL ABSTRACT
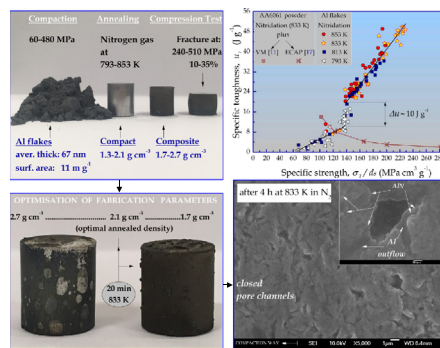
ABSTRACT

Modified aluminium foams, such as syntactic aluminium foams (SAFs) that contain tiny ceramic hollow spheres, are widely used for the protection of modern lightweight vehicles in mechanical impacts. Due to the typical compromises between strength and toughness, conventional SAFs absorb <5 J g^{-1} of mechanical energy before fracture.

In this study, we demonstrate that a nacre-like structure of piled aluminium flakes with in-situ grown AlN layers can provide a specific toughness of up to ~50 J g^{-1}. At the optimum toughness, the compressive yield strength $\sigma_{0.2\%}$, fracture strength σ_T and strain ε_T reach ≈110 MPa, 481 MPa and 0.35, respectively. The improved properties originate from the efficient nitridation-driven spreading of the partially melted Al of the flakes through the permeable nitride layers. In an N$_2$ atmosphere at about 833 K, an optimal composite structure is formed with a porosity ϕ_E and AlN volume fraction v_{AlN} of 0.26 and 0.12, respectively. The pre- and post-optimal annealing temperatures lead to a relatively small area of Al-AlN bonding, as a result of overgrowth and undergrowth of the AlN surfaces, respectively. This straightforward technology offers an affordable way to produce novel lightweight composites for state-of-the-art protection of vehicles and dynamic machinery in many industrial areas.

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1. Introduction

The economic and ecological benefits of using lighter but sufficiently rigid structures of aluminium foam in the construction and automotive industries are becoming more evident [1,2]. A good example is in lightweight vehicles, where hollow metal casings and frameworks are filled with an aluminium alloy foam to improve their resistance to mechanical impacts, however, the specific energy absorption (u) of such foams is itself limited to ≈4 J g^{-1}. Syntactic aluminium foams, where an Al alloy matrix encircles closely packed fine (100–1000 μm) ceramic hollow spheres (in particular, Al$_2$O$_3$ and Al$_2$O$_3$-SiO$_2$),

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are more efficient ($u \approx 5$–50 J g^{-1}) in the absorption of impact energy. An aluminium matrix of this type of foam can be formed by stir casting [3] and injecting [4–6] a liquid Al alloy or sintering an Al powder within the hollow spheres [7,8]. Nonetheless, the design of functional SAF components requires a metal casing due to these semi-brittle SAFs having a specific toughness u_T below 5 J g^{-1} [9,10]. Using even smaller average diameters $\overline{\delta}_\varnothing$ for hollow spheres, $\ll 100$ μm, could resolve the conflict between the fracture stress σ_T and the specific toughness u_T in SAFs. Nevertheless, it is technologically limited, when considering cost-effective methods of SAF manufacturing, in ensuring a uniformly distributed Al matrix with strong adhesion to the surface of alumina-based hollow spheres.

Alternatively, in-situ nitridation of compacted fine Al particles (e.g., AA6061, $\overline{\delta}_\varnothing \approx 13$ μm) followed by melting in a vacuum was undertaken for a novel type of SAF, achieving a fracture stress and a specific toughness of 193 MPa and 14 J g^{-1}, respectively [11]. These properties are attributable to a relatively uniform distribution of in-situ grown AlN shells ($\overline{\delta}_\varnothing \approx 5$–$20$ μm) within the Al alloy matrix. As is known, Al has stronger adhesion to the surface of AlN compared with Al$_2$O$_3$; the shear yield strengths $\tau_{0.2\%}$ in Al-A$_2$O$_3$ and Al-AlN interfaces similarly bonded at 1223 K are ≈ 35 MPa [12] and ≈ 57 MPa [13], respectively. More specifically, this method ([11]) proceeds via annealing of the compacted fine Al alloy powder at 833 K in a N$_2$ atmosphere for 6–24 h (optimally-12 h) for the in-situ growth of permeable AlN layers, in following the reaction below:

$$Al + 0.5N_2(g) \rightarrow AlN, \quad \text{the enthalpy change}, \Delta H_{830\ K} \approx -11.8 \text{ kJ g}^{-1}_{Al} \tag{1}$$
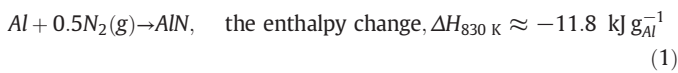
It was deduced in Ref. [14, 15] that the permeability of the growing AlN layers appears as numerous cracks due to significant differences between Al and AlN in the thermal expansion coefficients ($\alpha_{Al}\alpha^{-1}_{AlN} \approx 4.0$) and theoretical densities ($d_{AlN} d^{-1}_{Al} \approx 1.2$).

Thus, subsequent medium vacuum (~5 Pa) melting at 970 K for 2 h allows squeezing the liquid Al alloy through the cracked nitride shells and fill the interparticle channels. This additional vacuum melting (VM) process is relatively complex and expensive, although it imparts the necessary strength and toughness to the final product [11,16].

As an alternative to the VM process, the as-nitrided Al material can be crushed and consolidated through the severe plastic deformation in equal channel angular pressing (ECAP) [17].

More favourably, however, metal bonding of the AlN-shelled Al particles can be implemented during the in-situ nitridation process as follows. For instance, the enthalpy change ($\Delta H_{823\ K} \approx -31.0$ kJ g$^{-1}_{Al}$) during oxidation of a compacted ($\phi_E \approx 0.45$) Al powder with relatively small diameter ($\delta_\varnothing \approx 0.66$–$2.51$ μm) and high specific surface area ($A_s \approx 4.8$ m^2 g^{-1}) led to its temperature increasing from ≈ 823 K to above the Al melting point (≈ 933 K) [18]. The Al nitridation exoeffect ($\Delta H_{860\ K} \approx -11.8$ kJ g$^{-1}_{Al}$) of the same compacted powder caused penetration of the Al through the cracked 150-nm-thick AlN shells at 860 K [19]; in the porous Al powder compact, this process resulted in the AlN-shelled Al powder being strongly interconnected by the Al exudate.

The even greater specific surface area ($A_s \approx 11$ m^2 g^{-1}) of the piled Al flakes, with an average thickness $\overline{\delta}_t$ of 67.5 nm under a N$_2$ atmosphere at 870 K, can work as an effective driving force for penetration of the liquid Al through the AlN-shelled flakes [20]. On the other hand, the aligned AlN-shelled flakes bonded by aluminium constitute a nacre-like structure that can have exceptional fracture stress and toughness; nacre has ~0.5-μm-thick aragonite layers bonded by a biopolymer. Thus, the nitridation processes controlling the spread of aluminium
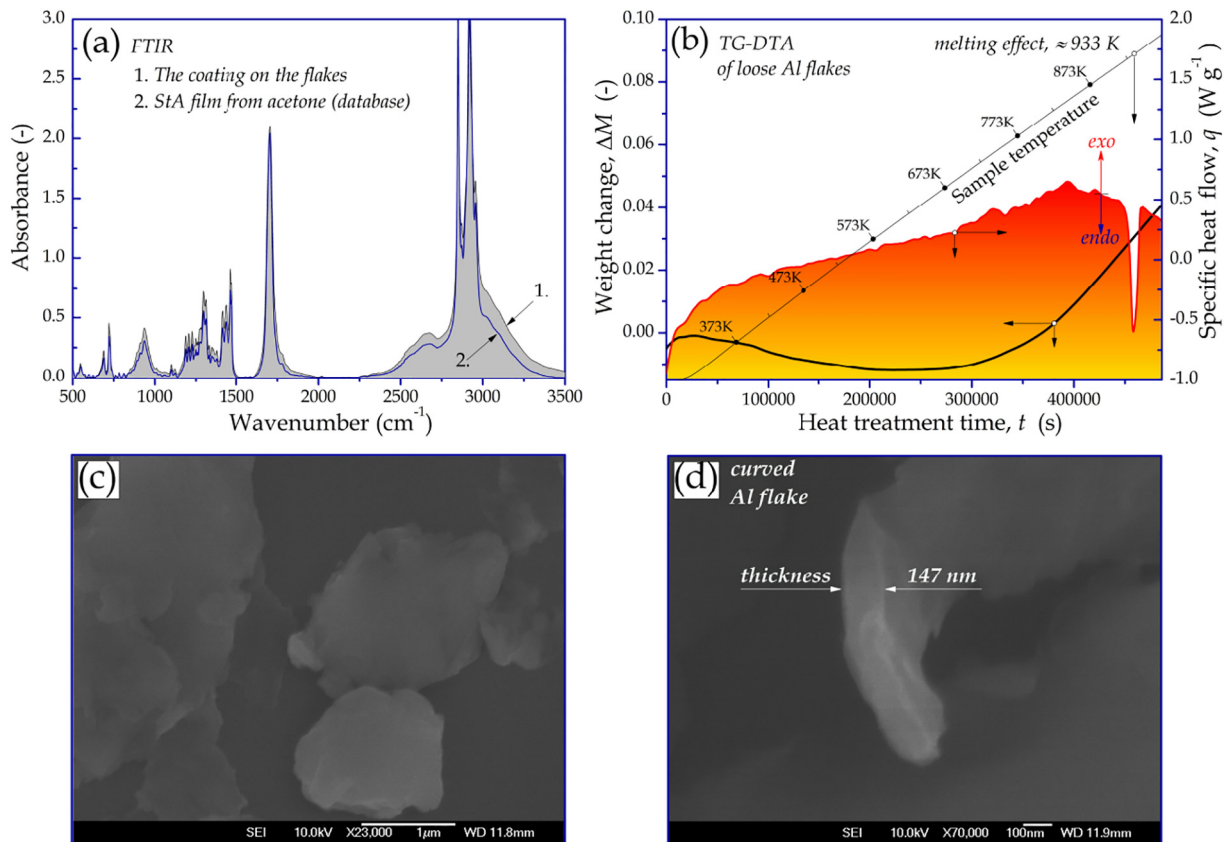

Fig. 1. (a) FTIR pattern of the Al flake film extracted by dissolving in acetone, (b) TG-DTA (5 K min^{-1}) thermograph of the as-received loose Al flakes in a nitrogen atmosphere, and (c), (d) top-view microimages of the separated Al flakes after thorough washing in acetone.