

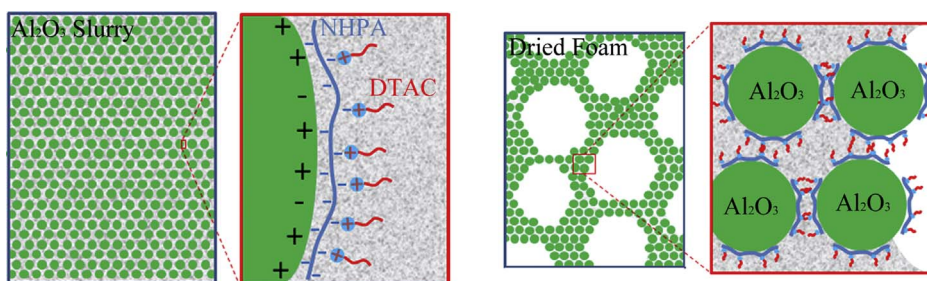


## Research paper

## Ceramic foams shaped by oppositely charged dispersant and surfactant

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Wet foams fabricated by direct foaming for use as ceramic foams are usually fixed with extra additives. Here, we fabricated alumina ceramic foams involving only an anionic dispersant (ammonium polyacrylate, NHPA) and a cationic surfactant (dodecyltrimethylammonium chloride, DTAC) without extra additives. DTAC interacted with the NHPA adsorbed on alumina particles and changed the zeta potential and hydrophobicity of the particles. In wet foam, the partially hydrophobic particles not only acted as foam stabilizers, but also formed a 3D network, which fixed the wet foam. By optimizing NHPA and DTAC concentration, alumina ceramic foam with high porosity (79.8%), small average cell size (50  $\mu\text{m}$ ) and high compressive strength (30.3 MPa) was obtained. This facile method is promising to fabricate any other ceramic foam due to its universal nature.

## 1. Introduction

Ceramic foams have been widely applied in many fields including thermal insulation, catalyst support, filter and medical implant thanks to their cellular microstructure [1,2].

Some processing methods such as replica technique and direct foaming have been developed to fabricate ceramic foams [3,4]. Direct foaming is an attractive method of preparing ceramic foams with open or closed cells. As the precursors of the ceramic foams, wet foams are

fabricated from ceramic slurries containing dispersant and surface-active materials such as surfactant and partially hydrophobic particle by direct foaming. Generally, the wet foams stabilized by surfactant are vulnerable to Ostwald ripening and coalescence, which exert considerable influence on the microstructure and properties of the resultant ceramic foams. To prevent these problems, wet foams are usually fixed by rapid gelation with organic additives such as acrylamide [5] and epoxy resin [6]. However, some of the additives are toxic [7] and extra additives cause long debinding time and more pollution. On the other

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hand, for the wet foams stabilized by partially hydrophobic particle [8–12], pH regulators such as HCl and NaOH are employed to endow particle surfaces with enough positive or negative charges, and short-chain amphoteric molecules such as butyric acid [8] and propyl gallate [13] are used to hydrophobically modify the particle surfaces. However, the shrinkage of wet foams during drying would induce formation of cracks, and this problem increases with sample size [14]. To prevent this problem, extra additives such as sodium alginate [8] and polyvinyl alcohol [9] are employed to generate physical or physicochemical gelation.

Here, we present a facile method of preparing ceramic foams that involves only a dispersant and an oppositely charged surfactant without any other gelling additive. The surfactant was used to hydrophobically modify the dispersant adsorbed on ceramic particles and to increase the hydrophobicity of the particles. The surfactant we chose would endow the particles with stronger hydrophobicity and hydrophobic interaction because it contains a 12-carbon hydrophobic chain which is longer than that of the short-chain amphoteric molecules used in the previous reports [8,13]. In the present work, taking alumina particles as an example, the surface chemistry of alumina particles, the rheological properties of alumina slurries and the microstructure and strength of alumina ceramic foams were examined and discussed. Crack-free and high-strength alumina ceramic foams were easily fabricated by tailoring the dispersant and surfactant concentration.

## 2. Materials and methods

### 2.1. Materials preparation

A commercial alumina powder (AES-11, Sumitomo Chemical, Tokyo, Japan;  $d_{50}$  0.45  $\mu\text{m}$ , purity 99.8%) was used as the raw material. The morphology of the alumina particles is shown in Fig. 1. Ammonium polyacrylate (A-30SL, Toa Gosei, Tokyo, Japan; denoted by NHPA) and dodecyltrimethylammonium chloride (QUARTAMIN 24P, Kao Chemical, Tokyo, Japan; denoted by DTAC) were chosen as the anionic dispersant and cationic surfactant, respectively. The concentration of NHPA and DTAC used in the experiments was relative to the mass of alumina powder. Ultrapure water was used throughout the experiments.

The process of fabricating wet alumina foams included the following steps: preparing alumina slurries with 50 vol% solids loading and different concentrations of NHPA by ball milling in a planetary mill for 1 h; adding DTAC into the slurries and mixing the slurries by ball milling for 30 min (Fig. 2a, DTAC modified the NHPA adsorbed on alumina particles); and generating wet foams via direct foaming with a kitchen mixer at 600 rpm for 4 min. Then the wet foams (Fig. 2b, alumina particles acted as stabilizers) were cast into plastic molds, demolded after 2–10 h of setting, and dried at room temperature for

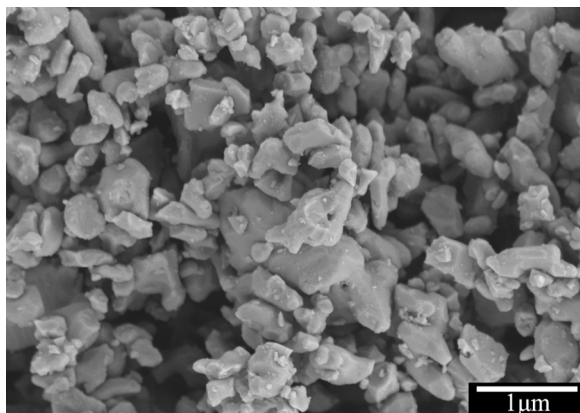


Fig. 1. The SEM micrograph of AES-11 alumina particles.

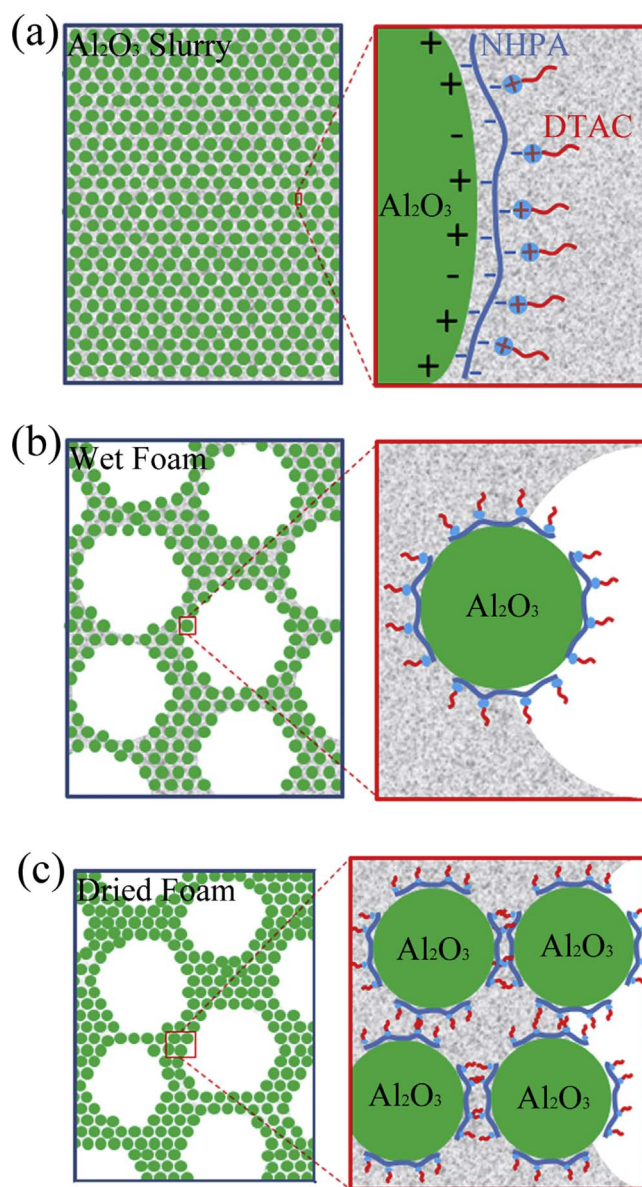


Fig. 2. Schematic illustration of alumina foams shaped by an anionic dispersant (NHPA) and a cationic surfactant (DTAC): (a) DTAC modified the NHPA adsorbed on alumina particles in alumina slurry, resulting in partially hydrophobic particles, (b) the particles acted as the stabilizers in wet foam and (c) formed 3D network in the dried foam.

2 days (Fig. 2c, 3D network in the dried foam). Finally, alumina ceramic foams were obtained by sintering at 1550  $^{\circ}\text{C}$  for 3 h.

### 2.2. Materials characterization

The effect of NHPA and DTAC concentration on the zeta potential of alumina particles in 0.2 g/L alumina suspensions was characterized using a zeta potential analyzer (Zetaplus, Brookhaven, NY, USA).

The effect of NHPA and DTAC concentration on the hydrophobicity of alumina particles was characterized via contact angle of a water droplet on alumina compact surface. The contact angle was determined by the sessile drop method using an optical tensiometer (Attension Theta, Biolin Scientific, Stockholm, Sweden) and fitting the droplet shape with the Young-Laplace equation. The alumina compacts were prepared from hydrophobically modified particles by cold isostatic pressing (200 MPa). The modified alumina particles were obtained by adding different amounts of DTAC to alumina slurries with 50 vol% solids loading and 0.24–0.40 wt% NHPA, mixing by ball milling, and

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