

# RECYCLING OF INDUSTRIAL AND NATURAL WASTES TO SiAlONs

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## Abstract

SiAlON ceramics were successfully produced from industrial wastes such as silicon sludge and aluminum dross by the nitriding combustion process. The silicon oxynitride as one phase in the sialons system was synthesized from desert sand as well. The nitriding combustion as an energy saving and recycling process, powder synthesis of SiAlONs, mechanical, thermal and chemical properties of the sintered products, and potential applications are reported.

**KEYWORDS:** Nitriding combustion, SiAlON, Silicon oxynitride, Recycle

## 1. INTRODUCTION

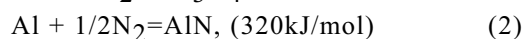
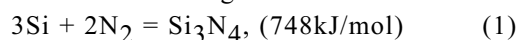
Combustion occurs by oxidation of carbon, hydrocarbons and hydrogen, and the global warming due to discharging carbon dioxide from the mass of combustion is an emergent issue. It is not well known, however, that combustion also occurs with nitrogen. Though nitrogen was believed as an inert gas for long years, various metal powders such as Si, Al, Ti, Zr, Nb, Ta burn with pressurized nitrogen over several atmospheric pressure [1]. This nitriding combustion is phenomenally similar to the oxidation combustion in respect to the highly exothermic reaction, but differs in leaving solid products of metal nitrides without discharging carbon dioxide.

The content of oxygen and nitrogen in air is about 20 vol%, and 78 vol%, respectively. The Clarke number of oxygen, silicon, and aluminum in the earth's crust is 49.5 wt%, 25.8 wt%, and 7.56 wt%, respectively. The major constituent of the air and the crust is oxygen, nitrogen, silicon and aluminum, though the metal elements exist in oxide forms. Therefore, these elements may be called as ecoelements.

On this viewpoint, we have investigated the nitriding combustion for the past two decades in order to develop an energy saving and low cost process to produce high performance nitride ceramics such as  $\text{Si}_3\text{N}_4$  [2], SiAlON [3], AlN [4], AlON [5], and  $\text{Si}_2\text{N}_2\text{O}$  [6, 7]. We have also applied the nitriding combustion for recycling of wastes to usable ceramics such as SiAlON formation from the silicon sludge discharged in silicon wafer production [8], and from aluminum dross discharged in aluminum smelting [9]. The  $\text{Si}_2\text{N}_2\text{O}$  was synthesized from desert sand as well. SiAlON is used for refractories in steel and metal foundry because of the chemical and mechanical stability at high temperature. This paper reviews our study on the synthesis and applications of SiAlON ceramics from the industrial and natural wastes by using the nitriding combustion process.

## 2. NITRIDING COMBUSTION

The nitriding combustion which we have investigated is based on the following two reactions.



These exothermic reactions propagate spontaneously and rapidly when the reactant is charged with a powder form in a pressurized nitrogen atmosphere over 0.5 MPa. In the lower nitrogen pressure, the nitrogen is not sufficiently supplied to sustain the combustion reaction. The combustion is initiated by passing a current of several tens of amperes through an ignition heater as shown in Figure 1.

The nitriding combustion was discovered by A.G. Merzhanov and his coworkers in 1967 as a solid-gas combustion mode of the self-propagating high temperature synthesis (SPHTS) [10]. Many other compounds such as carbides, borides, silicides, aluminides, and other compounds are produced from the mixture of metal and non-metal elements by SHS.

The nitriding combustion is regarded as an energy-saving process to produce various nitride ceramics because the synthesis reaction propagates spontaneously after the initiation of combustion. However, the preparation of raw metal powders and pressurized nitrogen is costly. It is important, therefore, how to produce higher performance materials or how to prepare metal powders with low cost. Our idea is to

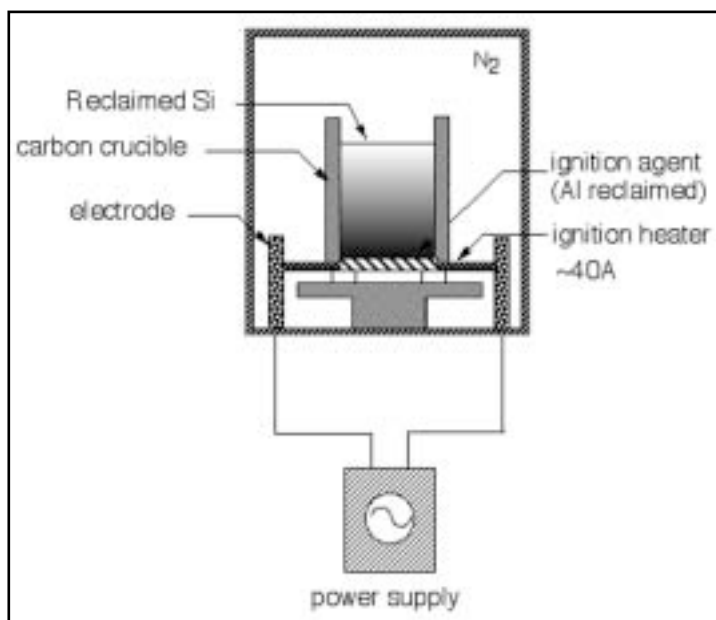
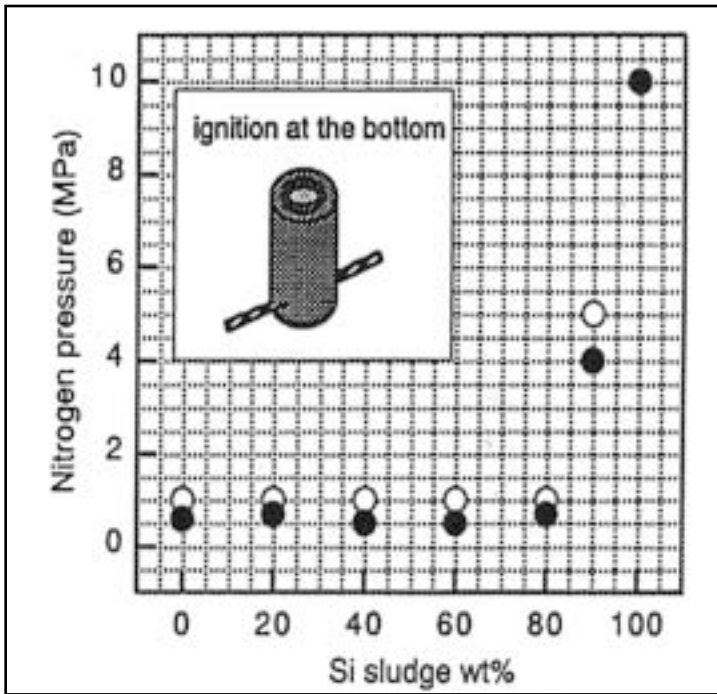


Figure 1. A schematic of autoclave for the combustion synthesis.



**Figure 2. Results of the nitriding combustion for the silicon sludge added with the reclaimed silicon and aluminum at different nitrogen pressures. The amount of aluminum addition is 10 wt% to the total amount of the silicon sludge and reclaimed silicon. Open circles; reacted. Closed circles; not reacted.**

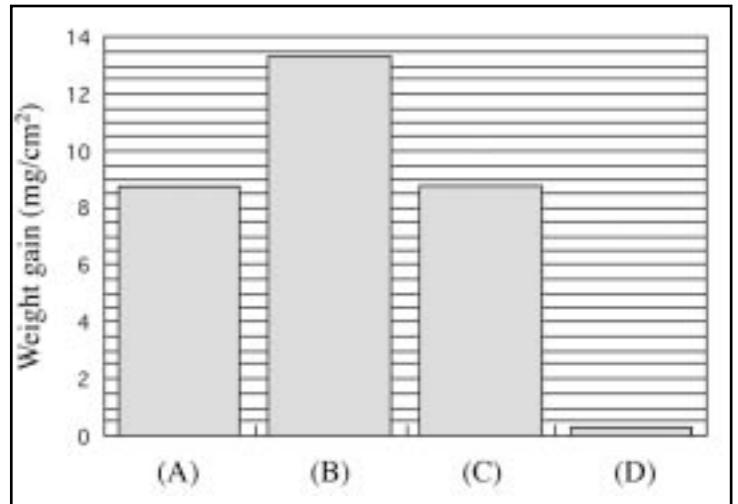
use reclaimed or by-product metal powders as the combustion agent to assist the nitriding combustion.

### 3. RECYCLING OF WASTES TO SiAlONs

#### 3.1 From Silicon Sludge to SiAlON

The output of semiconductor silicon for large-scale integrated circuits and memories in Japan is about 3,000 ton/year in recent years. It is produced as a single crystalline ingot and processed to wafers through cutting, polishing and washing. Large edges of a silicon ingot cut by trimming (~10% of an ingot) are used as a source material for polycrystalline silicon solar batteries. However, about 60% of an ingot after trimming is scraped with the wastewater disposal in cutting and polishing processes. This silicon sludge contains a lot of ceramic abrasives ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrSiO}_4$  or  $\text{ZrO}_2$ ), coagulants ( $\text{Ca}(\text{OH})_2$ ,  $\text{FeCl}_2$ , polymers), grinding oils, and water. It is disposed to a source of cement or to reclaiming lands. If the silicon sludge is left outside and dried, there is some fear of pollution by diffusing out of fine powders in air or fire. The recycling to high purity silicon is very difficult and costly.

We have applied the nitriding combustion to recycle the silicon sludge to nitride ceramics [8]. The silicon sludge used contains silicon (26 wt%),  $\text{Al}_2\text{O}_3$  wt% (14),  $\text{ZrSiO}_4$  wt% (31),  $\text{Fe}_2\text{O}_3$  wt% (27), and  $\text{CaO}$  wt% (2) after removal of volatile species at  $200^\circ\text{C}$ . The silicon content is too low to sustain the nitriding combustion. It is useful to add reclaimed silicon or aluminum powders to enhance the reaction. The dried sludge is pulverized, blended with these agents and then ignited in a pressurized nitrogen atmos-



**Figure 3. Results of oxidation test for sintered sialon recycled from aluminum dross. (A)  $1100^\circ\text{C}$ , (B)  $1200^\circ\text{C}$ , (C)  $1300^\circ\text{C}$ , (D)  $1300^\circ\text{C}$  (Post-heated in air at  $1300^\circ\text{C}$  for 5 hours.).**

phere. Figure 2 shows the result of the nitriding combustion for the silicon sludge as functions of added agents and nitrogen pressure. When the reclaimed aluminum is added as much as 10 wt% to the mixture of 80 wt% silicon sludge and 20 wt% reclaimed silicon, the nitriding reaction can occur at 1 MPa nitrogen pressure. The products consists of different phases SiAlONs, iron silicides, and zirconia, which are pulverized and sintered without sintering aids at  $1500^\circ\text{C}$  for 2 hours in nitrogen atmosphere. The flexural strength of product is 150 MPa which is compared to that of reaction sintered silicon nitride. It is stable at  $1200^\circ\text{C}$  in Ar atmosphere, but the oxidation promotes in air due to the existing of iron silicides inside. The sintered products can be used for abrasives, corrosion resistant filters, and wear resistant materials below  $1000^\circ\text{C}$ .

#### 3.2 From Aluminum Dross to SiAlON

Aluminum dross is discharged during the melting process for casting in aluminum industries. The surface of molten aluminum reacts with air resulting in formation of  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$ . The mixture of such oxides, nitrides, remaining aluminum and molten salts, which is called "aluminum dross," is usually buried in the ground. However, there is a fear of generation of harmful  $\text{NH}_3$  gas through the hydrolysis reaction of  $\text{AlN}$ . Though the recovery of aluminum and its alloys from the dross is investigated, the cost problem remains unresolved.

The result of the nitride combustion to recycle the aluminum dross is as follows [9]. The chemical composition of the aluminum dross used is  $\text{AlN}$  (75 wt%),  $\text{Al}$  (12 wt%),  $\text{Al}_2\text{O}_3$  (12 wt%), and a trace of impurities (Fe, V, Ti, Ca, Si, S, C). The lumps of the aluminum dross are crushed into powders and blended with the reclaimed silicon. The nitriding combustion can be sustained under 0.6 MPa nitrogen pressure by adding as much as 40 wt% of the reclaimed Si. The starting powders are converted completely to  $\beta$  SiAlON phases besides a small quantity of unreacted Si. The product powders can be sintered with the aids of  $\text{CaO}$ -

Al<sub>2</sub>O<sub>3</sub> at 1500°C in nitrogen atmosphere. The sintered body has a relative density corresponding to 80% of theoretical density. X-ray diffraction shows that a mullite (2SiO<sub>2</sub>·3Al<sub>2</sub>O<sub>3</sub>) layer is formed at the surface when post-heated the sintered products at 1300°C in air. Once the mullite layer is formed at the surface, no oxidation proceeds below 1300°C as shown in Figure 3. These results indicate that the mullite layer is uniformly formed and effective for oxidation protection.

### 3.3 From Desert Sand to Silicon Oxynitride

Silicon oxynitride, Si<sub>2</sub>N<sub>2</sub>O, is one of the phases in the SiAlONs system lying between Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>. It exhibits superior oxidation resistance to that of silicon nitride and silicon carbide especially at high temperatures [12]. Porous and dense Si<sub>2</sub>N<sub>2</sub>O components were developed by many research groups for refractory, heating elements, and high temperature engineering ceramics applications [13-18]. Among its reported production methods, up to now, there is no clear economic and reproducible process. This fact had limited the applications of Si<sub>2</sub>N<sub>2</sub>O as well as accurate characterization of its physical properties. The current conventional methods depend on heating silica with silicon (silicothermal reduction), silicon nitride (reaction sintering), or carbon (carbothermal reduction) in controlled nitrogen atmosphere at high temperatures for long periods of time. These conditions are economically undesirable and the Si<sub>2</sub>N<sub>2</sub>O product always contained impurity phases.

We have found an alternative promising method based on the nitriding combustion as an energy saving process and succeeded in synthesizing pure Si<sub>2</sub>N<sub>2</sub>O powder from a mixture of desert sand and reclaimed silicon under 3 MPa nitrogen gas [6, 7]. Desert sand is one of the most accessible natural resources around the world having high purities and low prices. The desert sand used is obtained from Sinai Peninsula in Egypt. It has high purity of > 99% and is pulverized to - 40 μm size. The nitriding combustion reaction is based on the following chemical equation:



The addition of 10 wt% Si<sub>2</sub>N<sub>2</sub>O powder to the starting mixture can promote the formation of homogeneous Si<sub>2</sub>N<sub>2</sub>O with no residual silicon. The synthesized powder consists of agglomerates of fine particles with sizes < 5 μm. The XRD pattern of the product shows strong peaks for silicon oxynitride with minor or negligible peaks corresponding to α-Si<sub>3</sub>N<sub>4</sub> as shown in Figure 4.

The sintered Si<sub>2</sub>N<sub>2</sub>O has comparable mechanical properties of the produced article sintered compact to the conventional Si<sub>2</sub>N<sub>2</sub>O materials. The Vickers hardness and fracture toughness of the produced article sintered compact are 18.7 GPa and 3.3 MPa m<sup>1/2</sup>, respectively. The reported values for commercial products are 15-22 GPa in hardness and 2.5-6 MPa m<sup>1/2</sup> in toughness [14,16,17]. The three-point flexure strength measured at room temperature is 363 MPa and the reported values for Si<sub>2</sub>N<sub>2</sub>O bodies are 300-750 MPa [14-17].

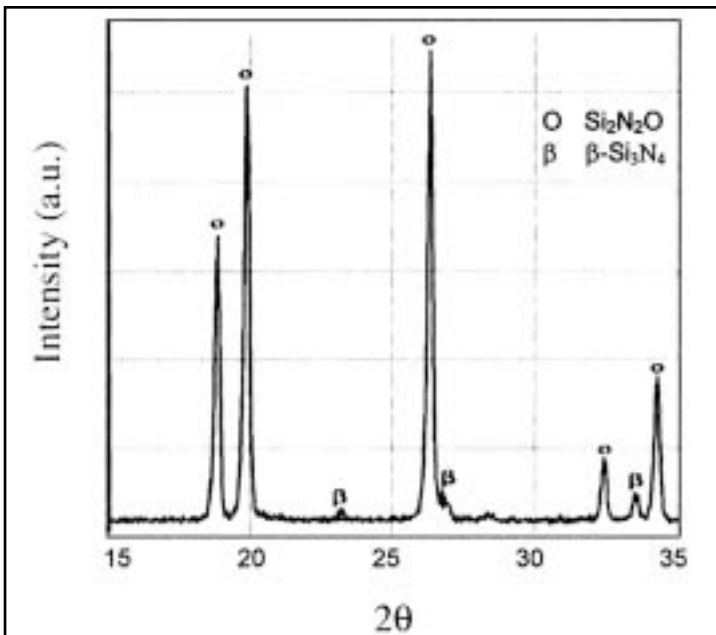


Figure 4. X-ray diffraction pattern of Si<sub>2</sub>N<sub>2</sub>O powder synthesized from desert sand.

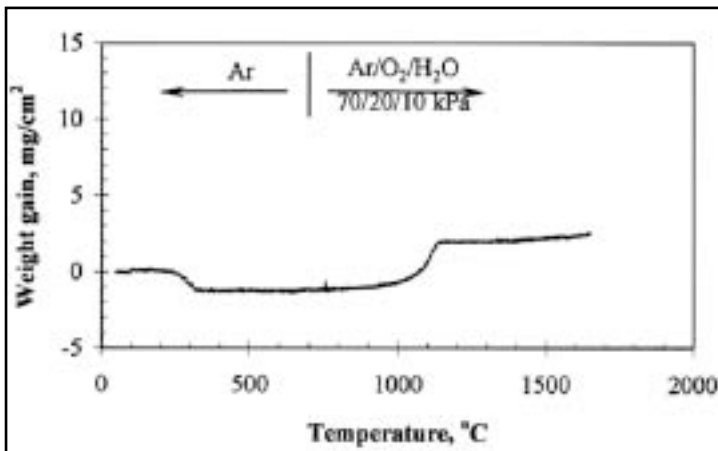


Figure 5. Weight gain of a porous Si<sub>2</sub>N<sub>2</sub>O compact during heating to 1500°C in Ar/O<sub>2</sub>/H<sub>2</sub>O atmosphere (70/20/10 kPa).

Test condition	Weight gain, mg/cm <sup>2</sup>
1200°C, 10 h	0.4
1400°C, 10 h	0.6
1500°C, 10 h	1.0

Table 1 shows oxidation results of this sintered compact after heating in dry air at 1200°, 1400°, and 1500°C for 10 hours. The material has excellent resistance at the temperatures up to 1500°C. Figure 5 shows the weight gain of a porous silicon oxynitride compact during heating to 1500°C in Ar/O<sub>2</sub>/H<sub>2</sub>O atmosphere. The specimen shows no weight gain until 1100°C, then had a little weight gain of 2 mg/cm<sup>2</sup>. The room temperature chemical resistance to the solutions 1M sulfuric acid, 2M sodium hydroxide, and 2M sodium chloride are almost infinitive for soaking periods reached 200 hours.

#### 4. CONCLUSIONS

The potential of the nitriding combustion has been studied in terms of an energy saving and recycling process to produce SiAlON ceramics. It is possible to convert both the silicon sludge discharged in silicon wafers production and the aluminum dross discharged in aluminum foundry to SiAlON ceramics. The monolithic Si<sub>2</sub>N<sub>2</sub>O ceramics can be synthesized from the mixture of desert sand and reclaimed silicon as well. It is desired to find useful applications of these recycled SiAlONs in powder, porous and dense forms.

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