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Synthesis of Advanced Ceramic Compounds By Intercalation

UNITED STATES DEPARTMENT OF THE INTERIOR



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Report of Investigations 9603

Synthesis of Advanced Ceramic Compounds By Intercalation

By Kyei-Sing Kwong and James P. Bennett

**UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary**

**BUREAU OF MINES
Rhea Lydia Graham, Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | |
|-------------------|-----------------------|
| Å | angstrom |
| °C | degree Celsius |
| g | gram |
| h | hour |
| μm | micrometer |
| mL | milliliter |
| min | minute |
| pct | percent |
| m ² /g | square meter per gram |
| wt pct | weight percent |

THE SYNTHESIS OF ADVANCED CERAMICS COMPOUNDS BY INTERCALATION

By Kyei-Sing Kwong¹ and James P. Bennett²

ABSTRACT

The U.S. Bureau of Mines investigated the synthesis of advanced ceramics ($\text{SiC}+\text{AlN}$, SiAlON , $\text{SiC}+\text{Al}_2\text{O}_3$, and $\text{Si}_3\text{N}_4+\text{AlN}$) from natural clays (kaolin, halloysite, or montmorillonite) by an intercalation and heat treatment method. This process includes the steps of refining a clay, intercalating organic chemicals into its layered structure, drying the intercalated mixture, firing the treated structure at certain temperature ranges in controlled atmospheres to form desired compounds, and grinding the loosely agglomerated structure. Focus of this research is to economically process advanced ceramic structures from abundant natural resources. The advanced ceramic phases produced in this simple treatment are homogeneously distributed at the nanostructure level, and may potentially lead to cost effective manufacturing processes.

The intercalation of clay was confirmed by X-ray and BET analyses. The evolution of chemical compositions during carbonization reactions and carbothermal reduction was investigated. The characteristics of refined clays and synthesized powders were studied. Advanced ceramic composites/solid solution have been produced from intercalated clays, without the presence of other compounds.

¹Ceramic engineer,

²Supervisory ceramic engineer, Tuscaloosa Research Center,
U.S. Bureau of Mines, Tuscaloosa, AL.

INTRODUCTION

LITERATURE REVIEW ON THE SYNTHESIS OF ADVANCED CERAMICS FROM PHYSICAL MIXTURES

Carbides and nitrides are known to have high hardness, high thermal conductivity, high heat resistance, good thermal shock resistance, high mechanical strength, and good chemical stability. These and other properties have brought about their increased use in advanced ceramic materials. Most high strength advanced ceramics contain the elements silicon, aluminum, oxygen, nitrogen, and/or carbon. One of these advanced compounds is SiC which is synthesized by several processes. These techniques include:

- 1) the direct reaction of silicon with carbon;
- 2) the carbothermal reduction of silica with carbon;
- 3) the vapor phase reaction of a hydrocarbon with silicon tetrachloride or silicon hydrides or other silicon compounds;
- 4) and the thermal decomposition of organic silicon polymers.

Similarly, there are several methods used to synthesize nitrides of silicon and aluminum. These include the following:

- 1) the direction nitridation of silicon/aluminum with nitrogen;
- 2) the vapor phase reaction between silicon/aluminum halides and ammonia;
- 3) the reaction between silica/alumina and ammonia;
- 4) and the carbothermal reduction and nitridation of silica/alumina with nitrogen.

Pure carbides and nitrides are very difficult to densify by sintering. Usually, an additive (sintering aid) is necessary to promote densification. The additions, however, degrade the performance of the ceramic material at high temperature. The use of carbides or nitrides with another phase to make composites such as SiC+Al₂O₃ and SiC+AlN or solid solutions such as SiAlON and SiC•AlN are other ways to densify these materials and improve their performance at high temperature.

There are several methods available to synthesize advanced ceramic composites or solid solutions from clays. Culter et al. mixed kaolin, carbon black and a catalyst of 1 pct iron together and fired the wet mixture at approximately 1,450 °C to synthesize SiAlON (1). Drawbacks of their method include: 1) the iron catalyst in their synthesis process reacts with silicon to form iron silicide, a low melting compound (MP. 1,200 to 1,500 °C) detrimental to the high temperature performance of SiAlON and 2) physical mixing of their process limits structural homogeneity within the matrix that is critical to making pure SiAlON. Because Culter et al used physical mixing, final product homogeneity was limited by the particle size of the starting raw materials (2).

Chaklader et al. mixed aluminosilicates and carbon in stoichiometric proportion by physical mixing and fired these above 1,550 °C in Ar gas to get a SiC+Al₂O₃ composite (3). They reported that the SiC morphology in the final composite was related to the morphology of the starting carbon source. For example, if graphite fiber was added, a SiC fiber would be synthesized in the sample and

if a spherical graphite particles were added, spherical SiC particles would be synthesized.

LITERATURE REVIEW OF THE INTERCALATION, CARBONIZATION PROCESSES, AND THE SYNTHESIS OF ADVANCED CERAMICS FROM INTERCALATED CLAYS

The performance of ceramic materials at elevated temperature is determined in part by their microstructure and composition. Homogeneity, particle size, and grain growth are three factors that influence the finished microstructure in ceramic manufacturing processes. The homogeneous distribution of compounds is always a problem in ceramic manufacturing processes. The homogeneous distribution of compounds and the particle size of starting materials may be avoided by taking advantage of the nanostructural distribution of elements in naturally occurring minerals.

Clays are naturally abundant layered minerals and have homogeneous chemical composition distribution. They may absorb some types of guest molecules in their interlayer space. These guest molecules may be controlled so as to contain types of organic carbon that support carbothermal reactions necessary to transform the clay into homogeneous advanced ceramic compounds. The absorption of these compounds into the clay structure may be a possible nanocomposite processing route for the production of homogeneous ceramic composites on a nanometer scale.

Natural clays include kaolin, halloysite, montmorillonite and etc. Montmorillonite has a higher ion exchange capacity and greater swelling capacity by water absorption than kaolin and halloysite. Because of this, montmorillonite is intercalated more easily with other compounds than kaolin or halloysite. Kaolin and halloysite layers are more difficult to open, but have been intercalated after treatment with entraining agents such as dimethyl sulfoxide, hydrazine, or formamid (4).

The homogeneity of a mixture of carbon and clay during intercalation plays an important role in the synthesis and purity of advanced ceramics compounds, such as SiC+AlN composites, SiAlON, SiC+Al₂O₃ composite, and Si₃N₄+AlN. Intercalation offers a novel route for producing nanocrystalline ceramics/composites by controlling the intercalation of clay particles with "guest" molecules on a nanometer scale. Subsequent thermal processing controls the structure produced. One critical area of intercalation is the "guest" molecules, which are required to supply enough carbon to perform carbothermal and/or nitridation reactions for the synthesis of advance ceramics. Organic molecules intercalated as "guests" can transform to carbon by heating under reducing conditions (carbonization). Depending on what is intercalated, low molecular weight paraffines, olifins and aromatics will volatilize first; followed by CO₂, CH₄, CO, and H₂ during the carbonization reaction. Carbonization is complete and residual carbon is left by 900 °C.

Instead of using physical mixing to synthesize Beta SiAlON, Chuzo Kato et al. used montmorillonite that was intercalated with polyacrylonitrile and reduced carbothermally (5). Their process involved treating montmorillonite with 0.01 to 0.02 N hexylammonium

hydrochloride solution three times, then immersing it and intercalating it with an acrylonitrile monomer for 24 h. The complex was then heated at 50 °C for 24 h to polymerize the acrylonitrile. The intercalation compound was heat treated for cyclization of the polyacrylonitrile in air at 220 °C for 48 h, then fired at 1,150 °C in a controlled atmosphere to get β -SiAlON, along with the small quantities of β -SiC and AlN.

Kato was awarded U.S. patent 4,652,436 for a method of making nitride and carbide materials by intercalating a monomer or prepolymer into the interlamellar space of a natural mineral such as clay (6) and thermally treating the materials. The treatment involved heating the intercalated clay-polymer complex at temperatures from 1,100 to 1,700 °C using a nitrogen or reducing atmosphere. The resulting carbide and nitride materials produced by this process include silicon carbide, titanium carbide, vanadium carbide, silicon nitride, aluminum nitride, molybdenum nitride, and SiAlON. The drawbacks of this process are: 1) the long process times; 2) the toxicity of acrylonitrile; 3) the complexity and cost of the process, and 4) the large quantity of volatiles from polyacrylonitriles (7).

Because of the large quantity of volatiles from most organic materials during carbonization, not enough residual carbon remains for most intercalation chemicals to support carbothermal reaction. This limits the selection of organic materials for intercalation and increases the manufacturing cost. These drawbacks were overcome in this study by using two chemicals with different functions. One intercalation chemical opens the interlayer space of the clay while the other acts as a source of carbon. The intercalation chemical acting as a carbon source carbonizes at a temperature lower than the evaporation temperature of the intercalation chemical, allowing additional carbon to deposit in the clay interlayer. The excess carbon forms carbides, nitrides, carbonitrides, and oxynitrides by the reaction of carbothermal and/or nitridation of clays.

The objective of this study is to synthesize nanostructured advanced ceramics by the intercalation of natural abundant clays using a simple treatment and cost effective manufacturing process. This report discusses the intercalation process, explains variables in the process and explains how to control the carbonization, carbothermal reduction and nitridation processes at elevated temperatures to produce different materials.

EXPERIMENTAL PROCEDURE

The intercalation and synthesis of advanced ceramics structures follows the process flow sheet in figure 1. Kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), montmorillonite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), and dehydrated kaolin ($\text{Al}_2\text{Si}_2\text{O}_7$) clays were evaluated in the intercalation process. Kaolin was supplied by Kentucky-Tennessee Clay Company, halloysite by New Zealand China Clays Limited, and montmorillonite by E.C.C. America, Inc. These hydrated clays were refined by the sedimentation method in water. Fifty g clays were stirred and ultrasonically treated in 1,000 mL of water for 30 min to break up the loose agglomerates and to disperse the clay as

slurries. The slurries were poured into 1,000 mL graduated cylinders and allowed to settle overnight. The suspended fine slurries were withdrawn from graduated cylinders and these were centrifuged to separate water and sediments. Only the top fine sediments, called refined clays, were collected and dried at 110 °C. Some refined kaolin was heated to transform to dehydrated kaolin ($\text{Al}_2\text{Si}_2\text{O}_7$) at 600 °C. Both refined and dehydrated clays were characterized by particle size analyzer, XRF (X-ray fluorescence), FTIR (Fourier Transform Infrared), XRD (X-ray Diffraction), BET, and TEM (transmission electronic microscope) to evaluate particle size, chemical compositions and impurities, crystal phases, surface area, and morphology.

INTERCALATION PROCESS

Chemical solutions were prepared for the intercalation of clays. In this study, the intercalation chemical was dodecylamine ($\text{C}_{12}\text{H}_{25}\text{NH}_2$) which is insoluble in water. HCl was added to dissolve the dodecylamine in water. Based on experiments, up to 0.6 mL 35 pct HCl can dissolve 1 g dodecylamine. In this research, 5 mL of 35 pct HCl was added to dissolve 1 g dodecylamine in order to increase the degree of intercalation. Sucrose was added to the dodecylamine/HCl solution. The sucrose was used to penetrate into the clay interlayer supplying additional carbon for carbothermal reduction. Generally, one gram of clay was intercalated with 1 g dodecylamine in 5 mL 35 pct HCl and from 0.6 to 1 g table sugar.

After the clays were mixed and treated with ultrasonic energy to break up agglomerates and to assist in the penetration of the intercalation chemicals into the interlayer structure, samples were prepared for XRD (X-ray diffraction) evaluation to confirm the existence of intercalation.

It is known that intercalation chemicals increase the d-spacing of the (001) plane and the surface area of clays (8). XRD was used to measure the d-spacing and to prove the existence of intercalation. It does not, however, give an indication of the degree to which it occurred. BET surface area measurements were used to give an indication of the degree of intercalation. These measurements were taken after calcination of the intercalated clays at 600 °C in inert gas followed by sample exposure at 600 °C in air. BET measurements also can indicate the effect of hydroxide bonds on intercalation, and the existence of intercalation after calcination of the treated clays at 500 to 900 °C through changes in the surface area. The calcined powders were analyzed by FTIR, and a carbon analyzer to study the evolution of intercalation chemicals, and the utilization of available carbon.

ADVANCED CERAMICS COMPOUND SYNTHESIS

Advanced ceramics compounds were synthesized under controlled atmospheres with different carbon content and firing temperatures. Table 1 lists process variables investigated in making advanced ceramics by clay intercalation. These variables include carbon content, firing temperature, atmosphere, and time. Because the intercalation chemical (dodecylamine) volatilizes before the

temperature where carbonization or carbothermal reduction occurs, four sugar concentrations (1, 0.7, 0.6, 0.5 g sugar per 1 g clays) were selected to synthesize SiC+AlN, SiAlON, and SiC+Al₂O₃. It is not known if complete volatilization of dodecylamine occurs during carbothermal reaction.

We can define total carbon concentration (TCC) as

$$\frac{\text{weight for theoretic carbon contents from dodecylamine and sugar}}{\text{total weight of clays, dodecylamine and sugar}}$$

Using this definition, the four sugar concentrations of 1, 0.7, 0.6, and 0.5 equal 39.9, 39.4, 39.3, and 39.2 pct total carbon concentration, respectively. Both total carbon concentration and sugar content will be used together in this paper for clarity.

Starting clay composition, firing temperature, dwell time and carbon concentration determine the types of product formed. From thermodynamic calculations and literature reviews, SiC+AlN can be formed by 1,600 °C and SiAlON by 1,400 °C. For this reason, the temperature range from 1,200 to 1,600 °C was selected in this study to process intercalated materials.

Over 100 samples were processed to evaluate the optimum conditions to synthesize advanced ceramics. After firing, the synthesized powders were characterized by XRD, TEM, FTIR, BET, XRF and particle size analyzer. This report will discuss the effect of factors and the optimum conditions for intercalation and synthesis.

RESULTS AND DISCUSSION

THE CHARACTERIZATION OF REFINED CLAYS

Table 2 lists characteristics of the refined clays as evaluated by XRF, particle size analyzer, BET, and TEM examination. Refined kaolin consists of an uniform (homogeneous) aluminosilicate composition but with variable potassium content and a trace of anatase (TiO₂). Refined halloysite is composed primarily of lath-shaped aluminosilicate particles with a trace of β -quartz. The lath-shaped halloysite may cause the average halloysite particle size to be much larger than those of kaolin and montmorillonite. Refined montmorillonite has complex non-uniform shape with higher SiO₂ and iron content than kaolin and halloysite. Refined montmorillonite has much higher surface area than refined kaolin and refined halloysite (Table 2).

EVIDENCE OF INTERCALATION

The absorption of intercalation chemicals into the clay layers may be influenced by the surface charge of the clays. Intercalation chemicals are thought to be absorbed on the ends of polar molecules (perpendicular) to highly charged clay surfaces and are thought to be attached parallel to low charged clay surfaces. X-ray diffraction studies indicated that interlayer spacing of intercalated dehydrated kaolin was 8.9 Å and that of the intercalated hydrated kaolin was 34 Å at room temperature. The

interlayer spacing for untreated kaolin is about 7.14 Å. This difference in spacing may be caused by the intercalation chemicals lying parallel on the surface of dehydrated kaolin and perpendicularly on the surface of hydrated kaolin.

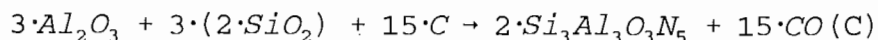
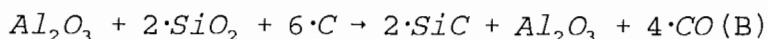
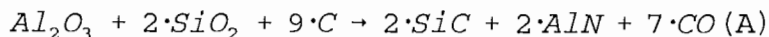
After treating halloysite and montmorillonite with the intercalation solution the halloysite basal spacing increased from 7.14 to 34 Å and the montmorillonite basal spacing increased from 15.7 to 17.7 Å. The increased interlayer spacing of all studied clays after intercalation proved that clays were intercalated.

The surface area of clays after intercalation and heat treatment ranged from 100 to 210 m²/g (from 7 to 15 times greater than untreated clays). This increased surface area is indirect evidence of the presence of intercalated material residue after carbonizing intercalated clays in the 500 to 900 °C temperature range. No significant increase in surface area of the clays was evident from the effect of sucrose and HCl without the intercalation chemical dodecylamine present.

As previously mentioned, kaolin and halloysite were intercalated after treatment by an entraining agent such as dimethyl sulfoxide, hydrazine, or formamid (4). In this study, kaolin and halloysite, however, were intercalated by using a dodecylamine-HCl complex without an entraining agent and they had swelled ability than montmorillonite as evidenced by d-spacing measurements.

THERMODYNAMIC CALCULATIONS

Thermodynamic calculations and material balances were conducted to evaluate possible reactions to synthesize advanced ceramic compounds. Equilibrium reaction equations assumed that the formation energy for kaolin equals the summation of formation energy for one Al₂O₃ and two SiO₂. Using this assumption, thermodynamic calculations indicate the reaction temperature, and carbon required to form ceramic composites in a N₂ atmosphere. The reaction temperatures, required carbon concentrations, and weight changes for different reactions from kaolin are shown in table 3.



THE CARBONIZATION STUDY OF INTERCALATED CLAYS

Intercalated samples of kaolin, halloysite, and montmorillonite containing 39.9 pct carbon (1 g sugar) were fired at 300, 500, 700 and 900 °C in N₂ gas for 1 h to examine the nature of bonding in the sample using FTIR. FTIR results indicated no change in bonding was detected through 300 °C. Between 300 and 500 °C, however, intercalated chemicals decomposed and by 700 °C, intercalated materials in kaolin and halloysite were completely

carbonized. Intercalated montmorillonite, however, had completely carbonized between 700 and 900 °C.

The calcined kaolin samples were analyzed for carbon content to indicate how much carbon remained after the carbonization processes. Residual carbon comes from heat treatment of intercalated clays in a reducing atmosphere to drive off volatiles and to cause carbonization of the intercalated chemicals. This information is shown in Table 4 for carbon concentration of intercalated clays fired at 500 and 900 °C. The data indicates that a significant amount of carbon was lost at temperatures up to 500 °C whereas only a small amount of carbon that was lost from samples fired at 900 °C. The cause of different residual carbon concentration in the samples may be due to the differing abilities of clays to carbonize sugar and dodecylamine at elevated temperatures.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to study thermal and weight loss behavior associated with chemical reactions in intercalated kaolin clays. Intercalated kaolin clays were dried at 110 °C overnight. DTA analysis shows that some evaporation of intercalation chemicals begins at about 300 °C (figure 2). The results from measurements of TGA, DTA, and carbon analysis suggest that carbonaceous components volatilized from kaolin samples in a range between 300 to 500 °C. TGA results indicated that about 35 pct of the starting weight of the intercalated sample remained after heating to 1,000 °C in an inert gas (figure 2).

Several intercalated clays were evaluated by TEM to obtain physical evidence of the location of carbon in the samples. Because of the limited capability of TEM, no evidence was obtained to show carbon presented in the interlayer of clays. TEM did not show, however, graphite or carbon agglomerates in the samples which contain about 20 wt pct carbon by carbon analysis. This indicates that carbon may be homogeneously distributed in the layered structure of the clays.

THE SYNTHESIS OF ADVANCED CERAMICS

XRD crystalline phase analysis (table 5) indicates different compounds are synthesized in different carbon concentrations, dwell times, and processing temperatures in a N₂ atmosphere. Generally speaking, the result in this table show that higher temperatures, increased carbon concentrations, and longer duration of heat treatment promote the formation of SiC+AlN. The XRD results indicate that a SiC+AlN composite could be synthesized at a temperature as low as 1,500 °C when processed for four hours in N₂ atmosphere and with a starting carbon concentration of 39.4 pct (0.7 g sugar).

SiAlON without other compounds present was synthesized by firing a halloysite clay at 1,450 °C for 2 hours in N₂ atmosphere using 39.3 pct carbon (0.6 g sugar). Several additional experiments were conducted using the same composition and higher and lower firing schedules in an attempt to reproduce SiAlON. The materials obtained in those experiments, however, contained not only SiAlON but also Si₃N₄ and/or Al₂O₃. The reason for this is being

investigated. These experiments indicate that the synthesis of SiAlON probably occurs in a very narrow set of processing conditions.

A SiC+Al₂O₃ composite was also synthesized at 1,550 °C in an Ar atmosphere with a total carbon concentration of 39.3 wt pct (0.6 g sugar). All the synthesized powders fired in N₂ and Ar atmosphere might contain excess free carbon. This free carbon can be removed by oxidation of the sample in air for 1 h at 500 °C.

THE CHARACTERIZATION OF SYNTHESIZED ADVANCED CERAMIC POWDERS

Advanced ceramic compounds produced by thermally processing intercalated clays were analyzed for carbon content, BET surface area, particle size by sedimentologic analysis, XRF crystalline phase analysis, and microstructure using the SEM and TEM. Table 6 shows the starting and final carbon concentration for intercalated clays fired in different environments. Only a small quantity of extra carbon remained in the samples which contained a major phase of SiAlON when the starting carbon content was 39.3 pct (0.6 g sugar) and when samples were fired at 1,450 °C for 2 h in N₂ gas.

All fired samples were ground by an agate mortar and pestle to break up the weak agglomerates that formed during firing. Sedimentographic analysis indicated these fine powders, after treated ultrasonically, were in the 2-3 μm particle size range. BET results (table 7) indicated that the halloysite had a larger surface area than kaolin and montmorillonite after intercalation with 39.9 carbon and processing at 1,600 °C for 1 h in N₂ atmosphere.

Figure 3A shows TEM micrograph of refined kaolin. The refined kaolin particles are typically hexagonal in shape with edges bounded by {010}- and {110}-type planes. In addition to kaolin, several discrete TiO₂ particles are present and were identified as tetragonal anatase by electron diffraction. Figure 3B shows the TEM micrograph of synthesized composites SiC+Al₂O₃. This composite was synthesized from intercalated kaolin with 39.3 initial carbon concentration (0.6 g sugar/1 g kaolin) at the firing temperature of 1,550 °C for 1 h in Ar environment. This composite material contains a wide range of sizes of whiskers and ribbons, irregularly-shaped particles of α and γ-Al₂O₃ and some small, round Fe-rich particles. In general, the whiskers are frequently single SiC crystals and the ribbons are more often polycrystalline. Small round Fe-rich particles indicate the firing temperature may be higher than the melting point of these particles.

X-ray Energy Dispersive analysis indicated that silicon was always present in the AlN grains formed from intercalated montmorillonite with a starting carbon concentration of 39.4 pct (0.7 sugar/1 g montmorillonite) and processing condition of 1,500 °C for 4 h in N₂ gas. It is reported in the literature that a solid solution of SiC+AlN could be synthesized at temperatures above 1,800 °C from powders of SiC and AlN (10) and at 1,600 °C by intimately mixed starting materials (11). Because of the limited high resolution capability of TEM, no definitive indication was available regarding the formation of a solid solution of SiC+AlN.

The chemical composition of intercalated and thermally treated powders was semiquantitatively analyzed by X-ray fluorescence (XRF) and results are listed in table 8. The results indicated that the major impurities in the starting clay and the resulting advanced ceramic compounds were Ti and Fe. The relative quantity of these impurities did not change significantly during carbothermal reduction below 1,600 °C. Iron is considered detrimental because it reacts with silicon to form FeSi_x , a low melting phase observed by SEM and TEM. The low melting FeSi_x causes degradation of the high temperature physical properties of finished ceramic materials. Chemical analysis revealed that the silicon concentration decreased when samples were fired above 1,500 °C. This occurs because SiO forms and evaporates at that temperature, leading to a decrease in the SiC content of the finished materials. To address the purity and changing chemistry of the materials during carbothermal reduction, additional research is being conducted to control the carbothermal process which lead to the evaporation of SiO .

CONCLUSIONS

The USBM Tuscaloosa Research Center has developed a process for the synthesis of advanced ceramics ($\text{SiC}+\text{AlN}$, $\text{SiC}+\text{Al}_2\text{O}_3$, SiAlON , and $\text{Si}_3\text{N}_4+\text{AlN}$) from natural clays by an intercalation and heat treatment method. This process includes the steps of refining the clay, intercalating it, drying the intercalated mixture, and firing the intercalated structures in a controlled temperature and atmospheres to produce advanced ceramic compounds. X-ray crystalline phase analysis indicated that clays were intercalated and that specific ceramic composites without other compounds could be synthesized from them. The study of chemical analysis indicated that the clay impurities of Fe and Ti were also impurities in the resulting advanced ceramic compounds. Si compound was found to volatilize at temperatures above 1,550 °C. Carbon analyses indicated that a significant amount of carbon was lost up to 500 °C with only a small loss occurring from 500 to 900 °C. TEM evaluation indicated a homogeneous microstructure. Particle size analysis indicated loose agglomerates in the range of 2-3 μm size range were synthesized.

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Table 1.—Process variables investigated in making advanced ceramics from intercalated clays

| Variables | Range |
|------------------------------|--|
| Clay | Kaolin, halloysite, montmorillonite. |
| Sugar content | 0.5 to 1 g sugar/1 g clays. |
| Firing temperature | 1,200 to 1,600 °C. |
| Atmosphere | Ar, N ₂ , Ar + N ₂ . |
| Dwell time | 1 to 4 h. |
| Heating rate | 11 °C/min. |

Table 2.—The chemical and physical characteristics of refined kaolin, halloysite, and montmorillonite clays

| Characteristics | Kaolin | Halloysite | Montmorillonite |
|---|--|-----------------|-------------------------|
| Particle size, μm | 0.47 | 5.73 | 0.79 |
| Surface area, m^2/g | 16.44 | 39.0 | 57.2 |
| Chemical composition, pct: | | | |
| Si | 25 | 27 | 33 |
| Al | 24 | 22 | 11 |
| Ti | 1 | 0.4 | 0.5 |
| Fe | 0.4 | 0.2 | 4 |
| K | 0.3 | NA | 0.1 |
| Morphology: | | | |
| Composition uniformity | Variable 0-5 % potassium | Uniform | Uniform |
| Discrete particles | Tetragonal anatase (TiO ₂) | β -quartz | β -quartz Fe-rich |
| Shape | Uniform | Uniform | Complex |

NA Not available.

Table 3.—Reaction temperature, weight change, and required carbon concentration for the reaction of kaolin with carbon to produce specific products

| Product | Reaction route | Reaction temperature, °C | Theoretical required carbon conc. pct C/sample wt. | Weight changes pct weight loss/sample wt. |
|--------------------------------------|----------------|--------------------------|--|---|
| SiC+AlN . . | A | 1,600 | 29.6 | -55.5 |
| SiC+Al ₂ O ₃ . | B | 1,500 | 21.9 | -44.8 |
| SiAlON . . | C | 1,450 ¹ | 15.8 | -40.8 |

¹Data from literature review (9).

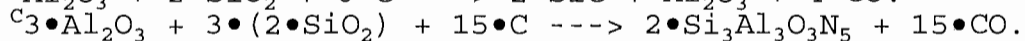
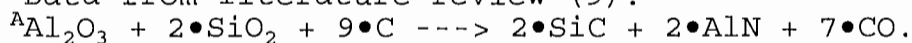


Table 4.—The final carbon concentration for different clay samples with an initial carbon concentration of 39.9 after thermal processing of 500 and 900 °C temperature for 1 h in N₂ atmosphere

| Temperature, °C | Clay | Final carbon, wt pct |
|-----------------|--------------------|----------------------|
| 500 | Kaolin | 14.9 |
| 500 | Halloysite | 17.6 |
| 500 | Montmorillonite . | 16 |
| 900 | Kaolin | 11.4 |
| 900 | Halloysite | 28.2 |
| 900 | Montmorillonite . | 24.5 |

Table 5.—Compounds synthesized in intercalated clays after thermal treatment in N₂ atmosphere

| Firing temperature, °C | Time, h | Clay | Compounds synthesized |
|---|---------|------|---|
| 39.9 wt pct TOTAL CARBON CONCENTRATION (1 g SUGAR/1 g CLAY) | | | |
| 1,200 | 1 | K | unidentified. |
| | | H | unidentified. |
| | | M | unidentified. |
| 1,400 | 1 | K | AlN, SiAlON, Si ₃ N ₄ . |
| | | H | AlN, SiAlON, Si ₃ N ₄ . |
| | | M | AlN, SiAlON, Si ₃ N ₄ . |
| 1,600 | 1 | K | SiC, AlN, TiN. |
| | | H | SiC, AlN. |
| | | M | SiC, AlN. |
| 39.4 wt pct TOTAL CARBON CONCENTRATION (0.7 g SUGAR/1 g CLAY) | | | |
| 1,300 | 1 | K | Mullite, amorphous. |
| | | H | Mullite, amorphous. |
| 1,400 | 1 | K | Mullite, amorphous. |
| | | H | Mullite, amorphous. |
| | | M | SiAlON, Al ₂ O ₃ , AlON. |
| | 4 | K | Al ₂ O ₃ , SiAlON. |
| | | H | Al ₂ O ₃ , SiAlON. |
| | | M | Si ₃ N ₄ , AlN. |
| 1,500 | 1 | K | SiAlON, Si ₆ Al ₁₀ O ₂₁ N ₄ . |
| | | H | SiAlON, Si ₆ Al ₁₀ O ₂₁ N ₄ . |
| | | M | SiAlON, Si ₃ N ₄ . |
| | 4 | K | SiC, AlN. |
| | | H | SiC, AlN. |
| | | M | SiC, AlN. |
| 39.3 wt pct TOTAL CARBON CONCENTRATION (0.6 g SUGAR/1 g CLAY) | | | |
| 1,500 | 1 | K | SiAlON, Al ₂ O ₃ , SiC. |
| | | H | AlN, Al ₂ O ₃ , AlON, SiC, Si ₃ N ₄ . |
| | | M | AlN, SiC, Al _{1.7} Si _{0.15} O _{2.85} . |

Table 5.—Compounds synthesized in intercalated clays after thermal treatment in N_2 atmosphere—Continued

| Firing temperature, °C | Time, h | Clay | Compounds synthesized |
|---|-----------|--------------------|--|
| 39.2 wt pct TOTAL CARBON CONCENTRATION (0.5 g SUGAR/1 g CLAY) | | | |
| 1,500 | 2 | K | Al_2O_3 , SiAlON, AlN, Si_3N_4 . |
| | | H | Al_2O_3 , SiAlON, AlN, Si_3N_4 . |
| | | M | SiC, AlN, $Al_{1.7}Si_{0.15}O_{2.85}$. |
| | 4 | K | SiC, AlN, Al_2O_3 . |
| | | H | AlN, Al_2O_3 , AlON, SiC, $SiAl_7O_2N_7$. |
| | | M | SiC, AlN. |
| 1,600 | 1 | K | AlN, AlON, SiC, Al_2O_3 . |
| | | H | SiC, AlN, AlON. |
| | | M | SiC, AlN. |
| H Halloysite. | K Kaolin. | M Montmorillonite. | |

Table 6.—Starting and final carbon concentration for intercalated clays fired in different processing environments

| Temperature °C | Process time, h | Clay | Gas | Starting carbon content, wt pct | Final carbon content, wt pct |
|-------------------|--------------------|------|----------------|------------------------------------|---------------------------------|
| 1,600 . . . | 1 | K | N ₂ | 39.4 | 4.65 |
| 1,600 . . . | 1 | H | N ₂ | 39.4 | 7.45 |
| 1,600 . . . | 1 | M | N ₂ | 39.4 | 14.9 |
| 1,450 . . . | 2 | K | N ₂ | 39.3 | 0.59 |
| 1,450 . . . | 2 | H | N ₂ | 39.3 | 0.27 |
| 1,450 . . . | 2 | M | N ₂ | 39.3 | 0.38 |
| 1,550 . . . | 1 | K | Ar | 39.3 | 6.33 |
| 1,550 . . . | 1 | H | Ar | 39.3 | 9.92 |
| 1,550 . . . | 1 | M | Ar | 39.3 | 15.1 |

H Halloysite. K Kaolin. M Montmorillonite.

Table 7.—Characterization of intercalated clays with 39.3 pct carbon (1 g sugar) processed at 1,600 °C in N₂ gas for 1 h

| Clay | Mean particle size, μm | BET surface area, m^2/g |
|-------------|-----------------------------------|---|
| K | 2.07 | 5.85 |
| H | 2.85 | 16.50 |
| M | 2.17 | 4.40 |

Table 8.—Chemical composition of the refined clays and synthesized powders

| Temperature °C | Time h | Gas | Starting carbon, wt pct | XRF measurement, wt pct | | | | | |
|-------------------|-----------|----------------|-------------------------------|-------------------------|----|------|-----|------|------|
| | | | | Si | Al | Ti | Fe | Ca | K |
| Kaolin | | | | | | | | | |
| refined . . | | | 0 | 25 | 24 | 1 | 0.3 | 0.02 | 0.1 |
| 500 . . . | 1 | N ₂ | 39.9 | 25 | 24 | 1 | 0.5 | 0.01 | 0.1 |
| 900 . . . | 1 | N ₂ | 39.9 | 25 | 23 | 1 | 0.5 | 0.01 | 0.1 |
| 1,450 . . . | 2 | N ₂ | 39.3 | 22 | 27 | 1 | 0.3 | 0.03 | 0.05 |
| 1,600 . . . | 1 | N ₂ | 39.4 | 13 | 37 | 1 | 0.3 | 0.02 | 0.01 |
| 1,550 . . . | 1 | Ar | 39.3 | 17 | 32 | 1 | 0.4 | 0.02 | 0.05 |
| Halloysite | | | | | | | | | |
| refined . . | | | 0 | 26 | 23 | 0.04 | 0.2 | NA | NA |
| 500 . . . | 1 | N ₂ | 39.9 | 27 | 22 | 0.08 | 0.2 | NA | NA |
| 1,450 . . . | 2 | N ₂ | 39.3 | 22 | 27 | 0.4 | 0.2 | NA | NA |
| 1,600 . . . | 1 | N ₂ | 39.4 | 14 | 37 | 0.07 | 0.1 | NA | NA |
| 1,550 . . . | 1 | Ar | 39.3 | 21 | 29 | 0.07 | 0.3 | NA | NA |
| Montmorillonite | | | | | | | | | |
| refined . . | | | 0 | 32 | 10 | 0.06 | 3 | 0.3 | 0.1 |
| 500 . . . | 1 | N ₂ | 39.9 | 34 | 10 | 0.1 | 4 | 0.3 | 0.1 |
| 900 . . . | 1 | N ₂ | 39.9 | 35 | 9 | 0.1 | 4 | 0.4 | 0.1 |
| 1,450 . . . | 2 | N ₂ | 39.3 | 32 | 15 | 0.2 | 2 | 0.3 | 0.1 |
| 1,600 . . . | 1 | N ₂ | 39.4 | 30 | 17 | 0.09 | 3 | 0.03 | NA |
| 1,550 . . . | 1 | Ar | 39.3 | 36 | 11 | 0.08 | 2 | 0.2 | NA |

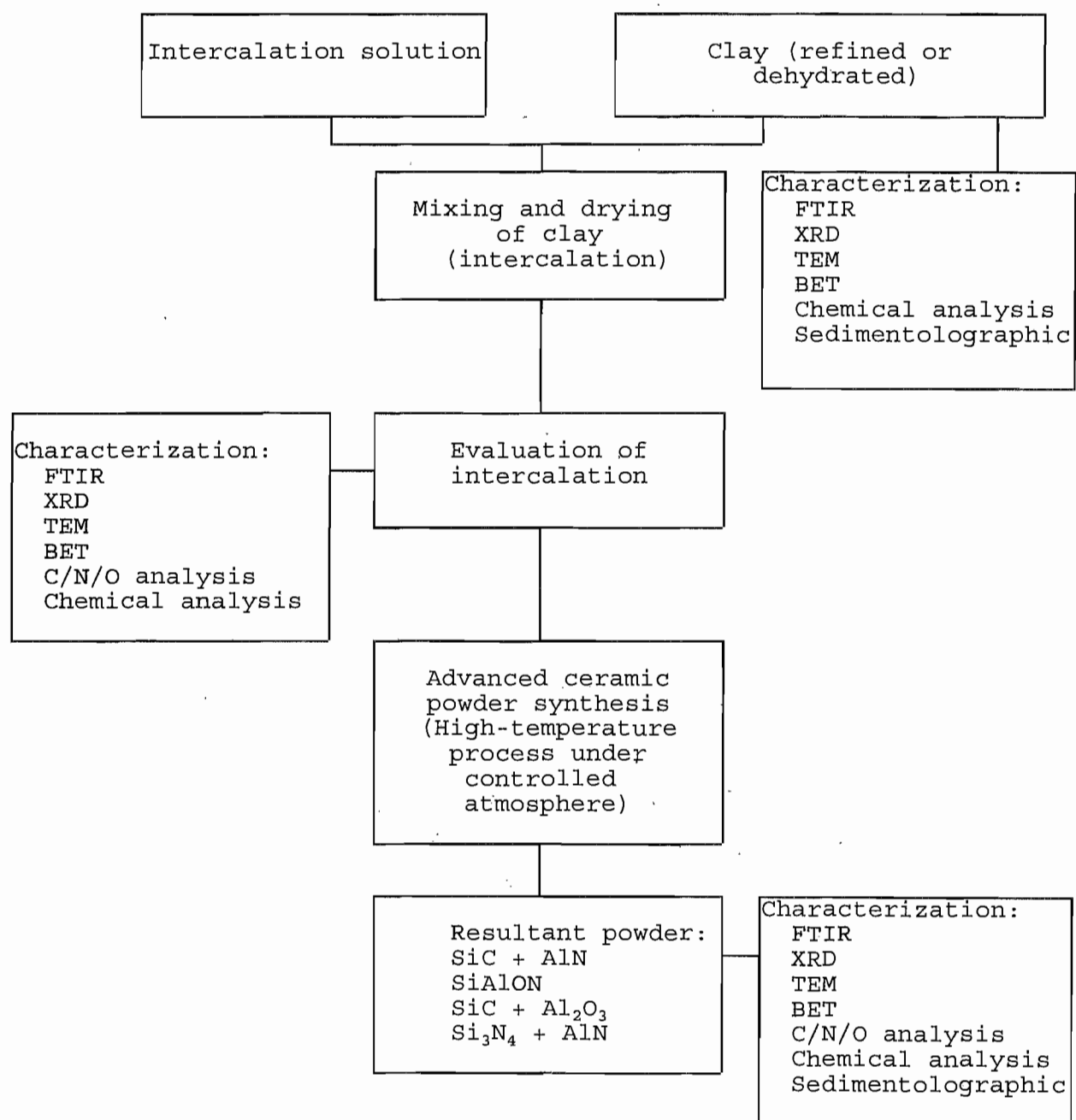


Figure 1.--Process flowchart for making advanced ceramics by intercalation.

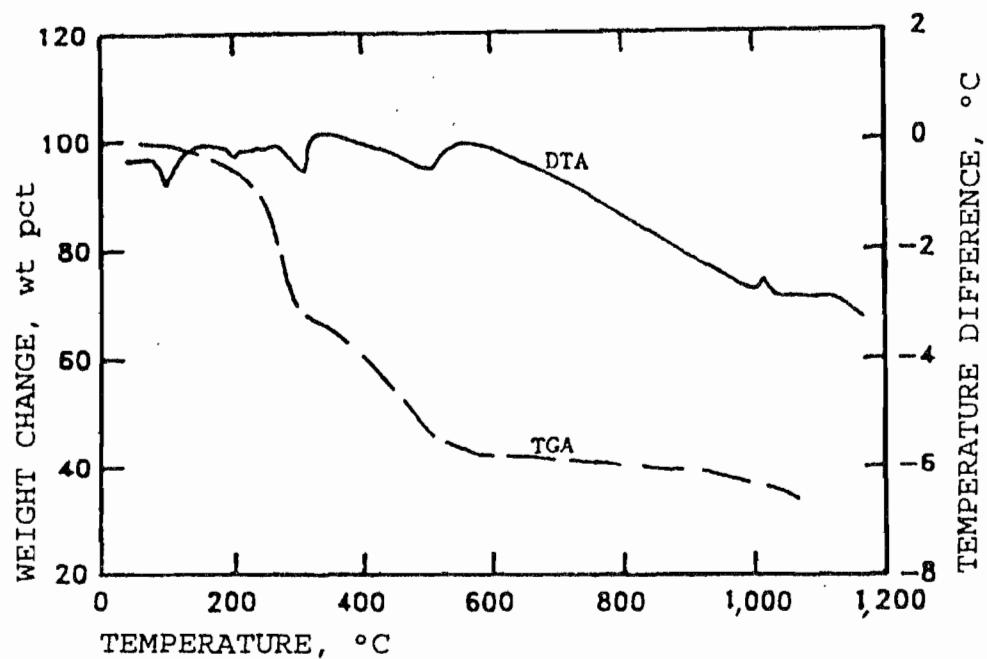


Figure 2.—TGA and DTA tests for intercalated kaolin from room temperature to 1,000 °C with a heating rate of 10 °C/min in N₂ gas.

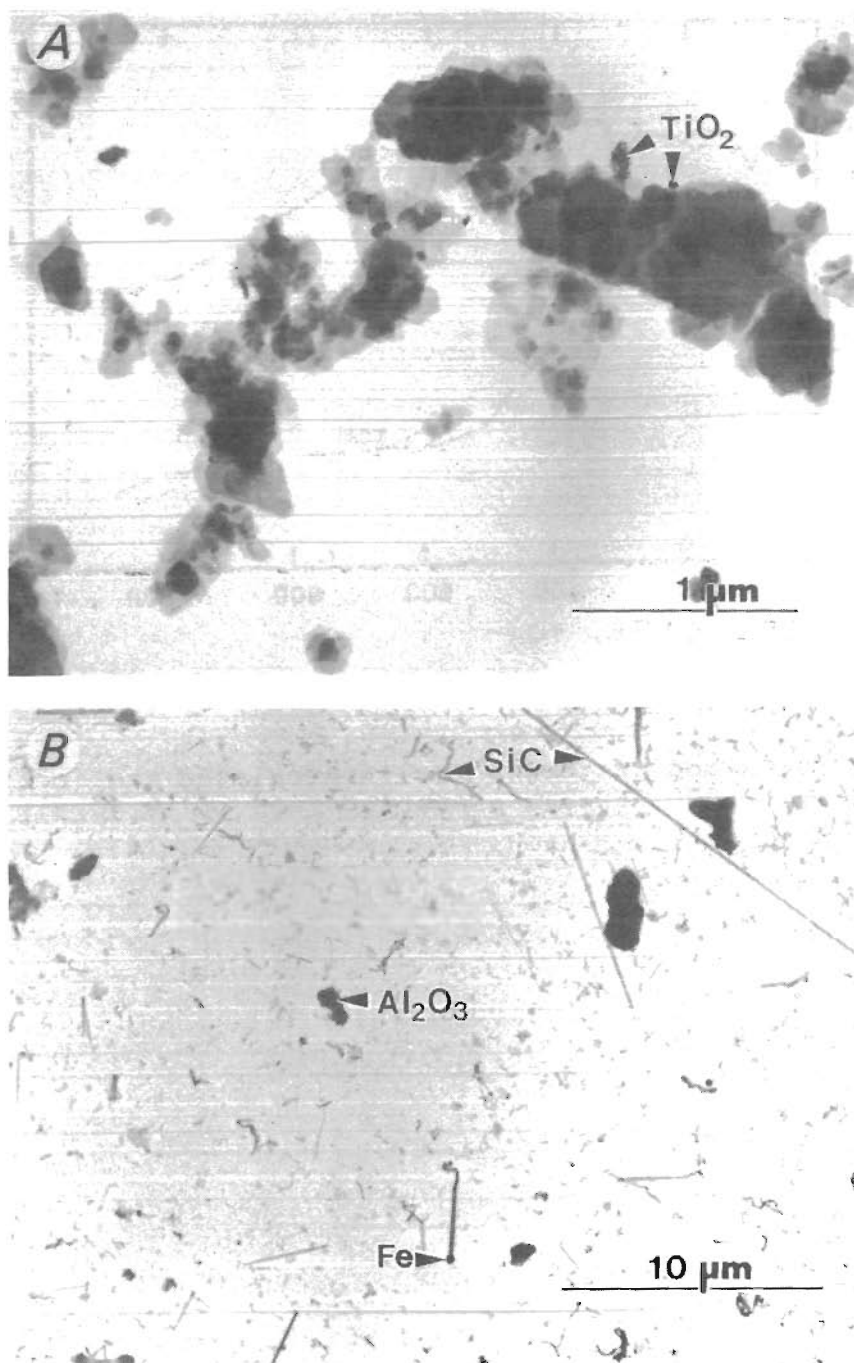


Figure 3.— The TEM micrography of (A) refined kaolin; (B) synthesized $\text{SiC}+\text{Al}_2\text{O}_3$ composite from intercalated kaolin with the 39.3 initial carbon content (0.6 g sugar) at the firing temperature of 1,550 °C for 1 h in Ar atmosphere.