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STUDIES ON THE USE OF SUPERCRITICAL AMMONIA FOR CERAMIC NITRIDE

SYNTHESIS AND FABRICATION

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ABSTRACT

The extractability of ammonium halides (including ammonium thiocyanate) formed as byproducts from the synthesis of $\text{Si}(\text{NH})_2$ via ammonolysis of the corresponding silicon tetrahalides using supercritical NH_3 as the extraction medium has been investigated. It was found that the NH_4SCN byproduct of ammonolysis of $\text{Si}(\text{SCN})_4$ can be almost completely extracted with SC ammonia from the insoluble $\text{Si}(\text{NH})_2$ forming a promising system for the synthesis of pure $\text{Si}(\text{NH})_2$, one of the best precursors to Si_3N_4 . In addition, it was found that Si_3N_4 , AlN , BN , and $\text{Si}(\text{NH})_2$ are insoluble in SC ammonia. Also discussed are design considerations for a supercritical ammonia extraction unit.

INTRODUCTION

Supercritical fluids (fluids above their critical temperature and pressure) are used as solvents and extraction media because of their near zero surface tension and good solvent properties. Very little has been reported on the use of supercritical (SC) ammonia as a solvent or extractant. This paper presents some preliminary results on the use of supercritical ammonia at temperatures and pressures up to 145 °C and 5500 psig as a solvent for refractory nitride synthesis.

The ability of a supercritical (SC) fluid to dissolve low vapor pressure solids was first reported by Hannay and Hogarth over 100 years ago (ref. 1). They demonstrated the dissolution of several salts such as cobalt chloride, potassium iodide and potassium chloride in supercritical ethanol ($T_c = 234$ °C, $P_c = 63$ atm). In 1896, Villard (ref. 2) published a review of the supercritical solubility phenomena. Carbon dioxide has been extensively investigated as a supercritical fluid because of its convenient critical temperature, $T_c = 31.1$ °C, and also because it is nontoxic, nonflammable, environmentally acceptable, and inexpensive. In addition, it is a good solvent for many organic compounds. Supercritical CO_2 has been used for coffee decaffeination, soybean oil extraction, extraction of chemotherapeutic agents from plant material and even ethanol-water separation (ref. 3). A general review of supercritical fluid extractions involving a variety of systems is reported in a recent issue of Reviews in Chemical Engineering (ref. 4).

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Supercritical solvents offer four advantages over conventional liquid solvents: (1) enhanced solubilities, (2) near zero surface tension, (3) high diffusivity and, thus, high mass transfer, and (4) low viscosity. Enhanced solubilities create a greater driving force for extraction. High diffusivity, low viscosity, and near zero surface tension of supercritical fluids are advantageous in extraction techniques because the fluid can easily penetrate small pores of a substrate.

Although little information has been reported on supercritical ammonia, supercritical water has been investigated extensively. For example, the dissolution of silicon dioxide in SC water has been demonstrated by Kennedy (ref. 5). The solubility of silicon dioxide in SC water is enhanced by the presence of a base such as sodium hydroxide. This system is now used to grow single quartz crystals (ref. 6). Surprisingly, very little has been reported on solvent properties of SC ammonia.

Based on an analogy with supercritical water as a medium in oxide and hydroxide chemistry, supercritical ammonia should make a good solvent for nitrides and amides. The analogous silicon nitride system would be SC ammonia as the solvent and sodium amide, NaNH_2 , as the corresponding base. It was this idea that prompted our investigation of the feasibility of using SC ammonia for ceramic nitride processing.

Currently, high purity silicon nitride is synthesized via the preparation of the silicon diimide precursor. Thermal decomposition of silicon diimide to silicon nitride occurs according to the reaction:



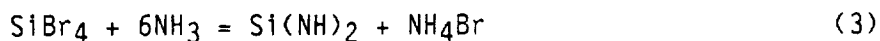
The pyrolysis of silicon diimide to silicon nitride is the basis of the Ubé process (ref. 7) from which high grade commercial silicon nitride is produced. The precursor silicon diimide is made by the reaction of silicon tetrachloride with dry ammonia.



The ammonium chloride is removed by extraction with liquid ammonia, and the insoluble silicon diimide is then thermally decomposed to silicon nitride.

Complete removal of the chloride from the diimide requires numerous extractions with liquid ammonia or long time periods of Soxhlet extraction with liquid ammonia (ref. 8). The remaining chloride impurity interferes with the pyrolysis of the silicon diimide because a series of reactions occurs requiring a higher temperature to remove the chlorine from the final product, silicon nitride (refs. 9 and 10). In order to synthesize pure silicon nitride at a lowered temperature, it is necessary to devise a more efficient way to extract the ammonium chloride byproduct. Extraction with supercritical ammonia was investigated with this idea in mind.

Other systems of silicon diimide synthesis may lead to purer silicon nitride product. Our preliminary work showed that in addition to the ammonolysis of silicon tetrachloride to produce silicon diimide, other reactions, equations (3) and (4), also may be used.



Although not demonstrated experimentally, it is assumed that the reaction of silicon tetraiodide with ammonia also forms silicon diimide and the corresponding ammonium halide, NH_4I .

In contrast to the reaction of SiCl_4 , SiBr_4 and $\text{Si}(\text{SCN})_4$ with ammonia, no silicon diimide forms in reactions of ammonia with silicon tetrafluoride or silicon tetraacetate. The conventional ammonolysis of silicon tetrafluoride, SiF_4 , leads to the formation of a volatile solid adduct, $\text{SiF}_4 \cdot 2\text{NH}_3$, which on sublimation yields no silicon diimide or silicon nitride. The addition product of silicon tetraacetate, $\text{Si}(\text{OCOCH}_3)_4$ and ammonia forms silicon dioxide instead of silicon nitride on thermal decomposition. Because these two compounds do not lead to silicon nitride, they were deleted from our SC ammonia investigation.

This paper includes descriptions of the experimental supercritical ammonia apparatus, procedures for the nitride solubility studies, and the studies of byproduct extraction in the synthesis of pure silicon diimide. The results of the nitride solubility studies are discussed. Then the results of SC ammonia extraction of byproduct ammonium salts (NH_4Cl , NH_4Br or NH_4SCN) from silicon diimide are presented along with those from the extraction of NH_4Cl from porous alumina beads. In addition, equipment design improvements are discussed.

EXPERIMENTAL

Nitride Solubility Experiments

The apparatus used to determine the solubilities of nitrides in supercritical ammonia (SC ammonia) consists of a modification of a high pressure autoclave (an Autoclave Engineers 300 cc vessel). A small crystallizing dish is suspended inside, in the top portion of the chamber well above the liquid ammonia level. The bomb is heated to 145°C which is above the critical temperature of ammonia, $T_c(\text{NH}_3) = 132^\circ\text{C}$. When a compound such as NH_3 is in its supercritical state, it occupies the complete volume of the container. If any nitride dissolves in the SC ammonia, some of the nitride will deposit in the suspended crystallizing dish when the temperature is lowered below the critical point and the liquid ammonia condenses in the bottom of the bomb. A deposit in the crystallizing dish would represent a soluble species. If none dissolves, then all of the nitride would remain at the bottom of the bomb. SEM and optical microscope photographs of the nitrides were examined before and after exposure to SC ammonia to detect any changes in particle structure which may indicate solubility and recrystallization of the nitrides.

First, a quantity of the nitride, alpha or beta Si_3N_4 , AlN or BN is added to the bomb, the bomb is then closed, and the specified amount of ammonia is condensed on top of the nitride. The solubility of Si_3N_4 was also investigated in SC ammonia containing the strong base sodium amide, NaNH_2 . This is accomplished by adding about 1 g of sodium shavings to the Si_3N_4 already in the autoclave. The chamber is immediately closed to minimize atmospheric reaction with the sodium. By the time supercritical conditions are reached, the sodium is converted to NaNH_2 according to the reaction



The conditions of pressure and temperature in the bomb, usually 145 °C at 4000 psig, were obtained by condensing the appropriate weight of NH₃ into the bomb, then heating the bomb to the desired temperature. For the specified conditions of temperature and pressure, the weight of ammonia to be condensed in the bomb can be calculated from the total volume of the container and the density of SC ammonia at that temperature and pressure. At the critical point $\rho(\text{NH}_3) = 0.235 \text{ g/cm}^3$ and at 145 °C and 4000 psig, $\rho(\text{NH}_3) = \text{about } 0.41 \text{ g/cm}^3$ (ref. 11). The weight of ammonia condensed in the bomb was determined gravimetrically by difference.

Supercritical Ammonia Extraction Unit

The supercritical ammonia extraction unit, illustrated in figure 1, is a modified version of the Autoclave Engineers supercritical carbon dioxide extraction unit. Ammonia is circulated via a positive displacement liquid metering pump (maximum P = 6000 psig) from the fluid supply cylinder to the system. Instead of the dip tube arrangement shown in figure 1, the supply system consisted of a small inverted cylinder from which liquid flows to the pump via its own vapor pressure. Constant pressure is maintained by a back pressure regulator. Because the heat of vaporization and the critical temperature of ammonia are higher than for carbon dioxide, a larger preheater vessel is required to vaporize the liquid ammonia and heating tapes are added to the system to maintain the specified temperatures above the critical point.

The extractor vessel was retrofitted with screens and glass wool to hold the solid sample in place during extraction. Upflow or downflow of solvent through the extractor vessel can be accomplished by appropriate valve adjustments. In all of our extractions we used the upflow mode. After extraction, the supercritical fluid solution flashes across a heated expansion valve into the separator vessel at atmospheric pressure where the dissolved solutes precipitate and the supercritical solvent expands to a gas which is vented through a flow meter to a fume hood.

Pressure is measured on both the high and low side of the pump. Temperatures are measured at many points along the system as shown in figure 1. Temperature is controlled by manually adjusting the appropriate reostat settings and the pressure is also adjusted manually using the back pressure regulator.

Preparation of Samples

Silicon diimide was synthesized by ammonolysis of a silicon tetrachloride or silicon tetrabromide solution in heptane, or silicon tetraisothiocyanate in toluene. Because of the hydrophilic nature of these silicon compounds, the procedures were carried out in a dry box where possible and care was taken to minimize exposure to atmospheric moisture. The ammonolysis of the silicon tetrahalide or tetraisothiocyanate yields a 4:1 molar ratio of the ammonium salt of the corresponding anion to silicon diimide, which is the precursor to silicon nitride. 90 wt % of the NH₄SCN was removed from the mixture formed by ammonolysis of the Si(SCN)₄ by extraction with acetonitrile saturated with NH₃

at 0 °C before SC extraction. This technique was not applicable to the ammonium halides. Pellets of the mixtures were manually pressed in a dry box to facilitate ease of handling. In addition to the salt and diimide, the pellets also contain some adsorbed organic solvent.

To determine the extractability of NH_4Cl with supercritical ammonia in the extraction system, ammonium chloride NH_4Cl was first absorbed into porous alumina beads. The alumina beads were dried at 144 °C for 24 hr, then vacuum impregnated with 5 M aqueous ammonium chloride and then dried again overnight at 110 °C. The amount of halide absorbed into the pellets was determined gravimetrically.

Reagent grade or equivalent chemicals were used. Liquid ammonia, anhydrous 99.99 percent, was supplied by Liquid Carbonic Corp. The silicon halides and isothiocyanate were obtained from Petrarch Systems, Inc. Silicon nitride, 325 mesh, 90 percent beta form and 325 mesh, 90 percent alpha form, used in the solubility experiments, was furnished by CERAC.

Extraction Procedures

The supply cylinder is filled with approximately 500 g of ammonia by distillation from a large cylinder rather than by direct liquid transfer. Distillation removes nonvolatile solids from the ammonia. To load the extraction vessel, it is removed from the system into the dry box where it is packed with sample pellets and quickly replaced back into the system. Because the silicon diimide/ammonium halide pellets are sensitive to atmospheric moisture, dry nitrogen was allowed to flow through the extraction section of the system to minimize atmospheric contamination until ammonia flow begins.

Initially, the system is filled with ammonia, then brought to equilibrium at the desired pressure and temperature under no-flow conditions. When the system pressures and temperatures are stabilized, the expansion valve is opened to the desired ammonia flow rate and extraction begins. The supercritical fluid solution is allowed to expand into the separation vessel where the solute is collected. The expansion valve and the back pressure regulator are manually adjusted throughout the extraction to maintain the desired temperatures and pressures.

For the silicon diimide/ammonium halide pellets, the extractions were done in batch wise steps until no significant amount of additional material was deposited in the separation vessel. Thus, during each extraction, the system was shutdown two to four times without removing the extraction vessel to evaluate the precipitant in the separation vessel. On the other hand, in experiments involving extraction of NH_4Cl absorbed on the inert porous alumina where quantitative rates are required, the extractions were carried out for specified times at a constant supercritical ammonia flow rate.

On completion of each extraction run, the extraction vessel was quickly removed to the drybox for sample recovery. The total amount of precipitant collected in the separator vessel, essentially ammonium salt, was determined by weighing in a closed weighing bottle. The composition was verified by x-ray diffraction and the quantity of halide was determined gravimetrically as the silver halide. Trace amounts of silicon were determined colorimetrically using the ammonium molybdate reagent.

The sample before and after extraction was evaluated for both halide and silicon content by chemical precipitation methods. The silicon diimide was precipitated as silicon dioxide by hydrolysis in dilute aqueous ammonia followed by ignition in air at 1000 °C. The ammonium halide was precipitated as the corresponding silver salt with silver nitrate. The presence of silicon diimide in the pellets was confirmed by the presence of silicon nitride after TGA analysis. From this analysis, the composition of the samples before and after extraction can be determined. Silicon diimide in those extracted pellets derived from $\text{Si}(\text{SCN})_4$ was determined by TGA (10 °C/min in N_2 up to 1200 °C) weight loss and the fact that the residue contained Si_3N_4 and no other detectable phases were verified by x-ray diffraction.

RESULTS AND DISCUSSION

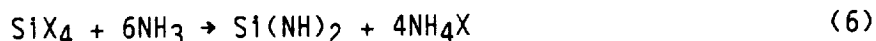
Nitride Solubility Experiments

At first SC ammonia was investigated for use in processing ceramic nitrides based on dissolution of nitrides, especially Si_3N_4 in SC ammonia. This idea was based on the analogous supercritical water/ SiO_2 system whereby solutions of SiO_2 in SC water are used to grow large single crystals of quartz (ref. 5). Unfortunately, no evidence was found that indicated any solubility of Si_3N_4 , AlN and BN in SC ammonia after 12 hr at 145 °C, 4000 psig. This was shown by the observation that no nitride was found in the crystallizing dish suspended inside of the bomb chamber at the end of the run. When the strong base, NaNH_2 was added to SC ammonia containing Si_3N_4 , a thin film was seen on the crystallizing dish. This highly alkaline film was found to contain no silicon and was probably sodium hydroxide derived from the immediate hydrolysis of the NaNH_2 when the opened bomb was removed from the dry box. Apparently, NaNH_2 is slightly soluble in SC ammonia. The insolubility of Si_3N_4 , AlN and BN in SC ammonia was verified by examination of SEM microphotographs; no difference in particle morphology was observed before and after exposure to SC ammonia for 12 hr at 145 °C and 4000 psig. An example of the particle structure before and after exposure is shown in figure 2. The lack of solubility is indicated by the retention of the rough edges on the nitride particles after exposure to SC ammonia. Even if the nitrides were slightly soluble in SC ammonia, the rough edges would be eroded or smoothed out. In cases of moderate solubility, some well defined crystals would be observed due to recrystallization.

In extraction runs presented later, even silicon diimide, $\text{Si}(\text{NH})_2$, was found to be insoluble in SC ammonia. Based on analogy with aqueous chemistry where hydroxides or hydrated oxides tend to be more soluble in water than anhydrous oxides, one would expect that amides, imides or ammoniated nitrides would be more soluble in SC ammonia than unsolvated nitrides. Because silicon diimide is not soluble in SC ammonia, the use of SC ammonia as an extraction vehicle for the purification of $\text{Si}(\text{NH})_2$ prior to pyrolysis and formation of Si_3N_4 was investigated.

Purification of $\text{Si}(\text{NH})_2$ Via SC Ammonia

$\text{Si}(\text{NH})_2$ is prepared by the reaction of the silicon tetrahalides: SiCl_4 , SiBr_4 , SiI_4 , and the tetraisothiocyanate, $\text{Si}(\text{SCN})_4$ with ammonia according to the equations



The function of the SC ammonia is to extract the ammonium salt byproduct and leave the insoluble $\text{Si}(\text{NH})_2$ residue. We anticipated high byproduct solubility in SC ammonia because the ammonium salts of interest are very soluble in liquid ammonia.

The extraction results for the $\text{Si}(\text{NH})_2 + \text{NH}_4\text{X}$ mixtures are found in table I. The initial sample mixture contains some absorbed organic solvent. For example, the pellets that contain NH_4Cl also contain about 24 percent toluene. In pellets containing NH_4Br , the toluene accounts for about 13 percent of the weight of the pellets, whereas those containing NH_4SCN contain 46.5 percent by weight acetonitrile. Thus, the reported composition of each sample is normalized based on the molar percent of $\text{Si}(\text{NH})_2$ and NH_4X without solvent.

The table gives the mole ratio of halide to silicon before and after extraction. Prior to extraction this mole ratio should be $\text{X/Si} = 4.00$. For the halides SiCl_4 and SiBr_4 , the ammonolysis was done in toluene solution, but for $\text{Si}(\text{SCN})_4$, acetonitrile, CH_3CN , was used as the solvent. Most of the NH_4SCN (90 percent by weight) was removed because of its solubility in $\text{CH}_3\text{CN} + \text{ammonia}$. In preliminary experiments, it was found that NH_4SCN is soluble in polar organic liquids such as pyridine, tetrahydrofuran and CH_3CN all saturated with ammonia. During ammonolysis of $\text{Si}(\text{SCN})_4$ dissolved in CH_3CN most of the NH_4SCN dissolved in the $\text{CH}_3\text{CN}/\text{NH}_3$ solution leaving the $\text{Si}(\text{NH})_2$ precipitate with most of the NH_4SCN removed. The solubility of NH_4SCN in polar organic liquids containing ammonia should be anticipated because of its high solubility in liquid ammonia, 312 g per 100 g of ammonia at 25 °C under unspecified pressure (ref. 12). For this case, the initial pseudo halide to silicon ratio used in the SC ammonia extraction was 0.185.

The presence of an oily substance in the separator vessel after the first stage of extraction indicates that SC ammonia removes the organic solvent in addition to the ammonium salt. Also observed in the NH_4Cl run was a brown discoloration of the $\text{Si}(\text{NH})_2$ residue in the extractor. After removing the silicon species as SiO_2 from the acid hydrolysis of the $\text{Si}(\text{NH})_2$ residue, addition of NH_4OH to the aqueous solution precipitated a rust colored substance identified as hydrated Fe_2O_3 . The amount corresponds to a Fe/Si mole ratio of 0.236 which is equivalent to about 21 percent by weight. The impurities account for 20 to 30 wt % of the extracted residue. The iron contamination is attributed to attack of the stainless steel sample supports in the extractor by the acid solution of NH_4Cl in SC ammonia. Rusting of these screens was also noted.

For the ammonium chloride pellets, the normalized mole percent of $\text{Si}(\text{NH})_2$ increased from 19.1 to 78.9 percent and the NH_4Cl decreased from 80.9 to 21.1 percent after extraction with supercritical ammonia at 145 °C and 5000 psig. The extraction process removed 93.2 percent of the ammonium chloride. For the ammonium thiocyanate pellets, the normalized mole percent of $\text{Si}(\text{NH})_2$ increased from 84.4 to 100 percent and the NH_4SCN decreased from 15.6 to 0 percent resulting in 100 percent of the salt removed. For the ammonium bromide pellets, the normalized mole percent of $\text{Si}(\text{NH})_2$ increased from 19.8 to 69.4 percent and the NH_4Br decreased from 80.2 to 30.6 percent resulting in an 89 percent removal of the ammonium bromide.

Table II gives data on an estimate of the utilization efficiency of SC ammonia to extract NH_4Cl , NH_4SCN , and NH_4Br respectively. Unfortunately, losses within the system, NH_3 loss at the pump, and awkward construction of the apparatus precluded a rigorous quantitative material balance.

The extraction efficiency, especially concerning NH_4Cl and NH_4Br , is low in relation to their high solubility in liquid ammonia. The low extraction efficiency for these ammonium halides may be due to the relatively low density of SC ammonia at 145°C , 5000 psig compared to that of liquid ammonia; the solubility of these salts in SC ammonia is not as great as expected. This conclusion is also supported by our next set of experiments concerning the extraction of NH_4Cl absorbed in porous alumina beads.

The removal efficiency for the thiocyanate system is about 150 percent higher than for both the chloride and the bromide containing mixtures. Unlike the chloride or the bromide mixture, we also show that the NH_4SCN can be completely removed.

A factor contributing to the relatively low solubility of NH_4Cl and NH_4Br in SC ammonia may be the formation of a less soluble triammoniate in the presence of excess ammonia. Morgan (ref. 13), in his investigation of the extraction of NH_4Cl from the $\text{Si}(\text{NH})_2 + \text{NH}_4\text{Cl}$ mixture formed by ammonolysis of SiCl_4 , found that even a week of continuous Soxhlet extraction with liquid ammonia did not completely remove all the Cl^- ion from the $\text{Si}(\text{NH})_2$; 0.1 percent remained. He suggested that in the presence of ammonia, NH_4Cl forms a triammoniate which is less soluble in NH_3 . We also do not exclude the idea that some of the halide may be chemically bonded to the silicon species making it more difficult to extract.

According to our evaluation of the three routes to $\text{Si}(\text{NH})_2$, the most promising for the preparation of this precursor to Si_3N_4 is via the ammonolysis of $\text{Si}(\text{SCN})_4$. Our results show that the pure precursor material can be made by this method followed by the extraction of the readily soluble NH_4SCN .

The bulk of the NH_4SCN byproduct was removed by decantation of the $\text{NH}_3\text{-CH}_3\text{CN}$ solution from the $\text{Si}(\text{NH})_2$ precipitate; then the remainder of the NH_4SCN was extracted with SC ammonia. On addition of water to the $\text{Si}(\text{NH})_2$ residue, hydrolysis occurred with the formation of insoluble $\text{SiO}_2\cdot\text{XH}_2\text{O}$. After removal of the $\text{SiO}_2\cdot\text{XH}_2\text{O}$ precipitate, addition of AgNO_3 to the acidified (with HNO_3) clear supernatant liquid, gave no visual evidence of a AgSCN precipitate thus indicating that no significant amount of NH_4SCN remained in the extracted $\text{Si}(\text{NH})_2$ residue. Based on the handbook value (ref. 14) solubility product of AgSCN , is 1.16×10^{-12} at 15°C .

Figure 3 gives the TGA of the pure $\text{Si}(\text{NH})_2$ derived from the ammonolysis of $\text{Si}(\text{SCN})_4$ dissolved in CH_3CN . The TGA shows a gradual loss in weight up to 1450°C at which point the sample is 81.4 percent of the original weight. This corresponds to a weight loss of 18.6 percent which is slightly less than the calculated theoretical weight loss of 19.5 percent when $\text{Si}(\text{NH})_2$ is thermally converted to Si_3N_4 according to the following reaction.



The dashed TGA curve on figure 3 is the TGA obtained by Morgan (ref. 13) for $\text{Si}(\text{NH})_2$ obtained from SiCl_4 and NH_3 . The NH_4Cl content was less than 0.1 percent. Both curves show a gradual weight loss with no indication of well defined intermediates. Other differences to be noted are that Morgan's $\text{Si}(\text{NH})_2$ was recovered from liquid ammonia whereas ours was exposed to a higher temperature (145 °C supercritical NH_3). The total weight loss, 23 percent, of Morgan's $\text{Si}(\text{NH})_2$ exceeded the theoretical 19.5 percent for the decomposition of pure $\text{Si}(\text{NH})_2$ to Si_3N_4 . This may be due to some NH_3 of solvation contained in Morgan's material which would add to the weight loss whereas our material, which was exposed to SC ammonia at a higher temperature of 145 °C intermediates forming nitride-imides of the type $\text{Si}_2\text{N}_2\text{NH}$ may have lost some of its NH_3 due to decomposition. This would give a less than stoichiometric weight loss.

On comparison with Morgans TGA which shows that $\text{Si}(\text{NH})_2$ is completely decomposed to the nitride above 1100 °C, we can assume that, in our TGA, all the diimide is converted to nitride at 1450 °C. Between this temperature and 1500 °C, the end of the TGA run, there is a sudden additional weight loss of 1.6 percent resulting in a final value of 79.8, corresponding to a 20.2 percent weight loss. However, in a separate experiment no additional weight loss occurred upon heating of the $\text{Si}(\text{NH})_2$ from 1500 to 1700 °C. This suggests that the TGA curve (fig. 3) would probably flatten out above 1500 °C. Although we are unable at this time to establish a definite cause for this sudden weight drop, this result is not thought to be characteristic of $\text{Si}(\text{NH})_2$ decomposition. Rather, we attribute this loss to the vaporization of SiO as a consequence of SiO_2 impurity in the sample; $\text{Si}(\text{NH})_2$ and its decomposition product intermediates are extremely sensitive to hydrolysis; thus, any reaction with atmospheric moisture during handling would result in SiO_2 contamination in the final product.

The residue remaining after the TGA was amorphous by x-ray diffraction. However, when the sample was heated to 1700 °C for 8 hr in N_2 , the amorphous material was converted to pure alpha Si_3N_4 according to x-ray diffraction analysis. Based on this result, it is logical to assume that the end-product of the TGA run was amorphous Si_3N_4 .

The synthesis of $\text{Si}(\text{NH})_2$ from $\text{Si}(\text{SCN})_4$ and NH_3 has advantages for the preparation of Si_3N_4 at a relatively low temperature which favors the formation of finely divided powder with high surface energy. Such powders are easily densified into useful articles.

Extraction of NH_4Cl From Porous Alumina Beads

To understand the effect of solvent parameters on extraction efficiency, a simple system involving NH_4Cl absorbed on to the inert substrate, porous alumina, was investigated at four SC ammonia conditions and one liquid ammonia parameter. These results are presented in table III and illustrated by plotting extraction efficiency, the percent NH_4Cl extracted, versus solvent density in figure 4. On examination of figure 4, it becomes apparent that solvent density influences extraction efficiency. The greatest extraction efficiency (91.6 percent NH_4Cl removed) was obtained at the highest density conditions tested, i.e., in liquid NH_3 at 50 °C and 4000 psig. The lowest efficiency (52 percent NH_4Cl removed) occurred at the lowest density conditions, near the supercritical point of NH_3 at 145 °C and 2000 psig. Increasing the density of

the extractant, NH_3 , enhances the extraction efficiency by increasing the solubility of the solute in the solvent.

There is considerable discussion explaining nonionic solute solubility in essentially nonpolar to slightly polar supercritical fluids, e.g., naphthalene in ethylene, and benzoic acid in CO_2 . McHugh and Krukonic (ref. 15) describe a relationship based on solute sublimation pressure to predict the solubility of nonvolatile, covalent solids in high density SC nonpolar fluids.

Unfortunately no such empirical relationship has been well developed to predict solubility of ionic crystalline solutes e.g., NH_4Cl in polar supercritical solvents such as ammonia.

In order to dissolve an ionic crystal, NH_4Cl , in a polar solvent, NH_3 , there must be an interaction between solute and solvent, which is solvation of the anion and cation, to break up the crystal into individual ions. Thus, the higher the solvent concentration, the more solvent molecules are available for interaction. With this fact in mind, the solubility of ionic solutes is expected to increase with increase in SC solvent density.

However, density or solubility is not the only parameter affecting the extraction efficiency as evidenced by its minimal change with density between points B and D. Mass transport properties such as diffusivity and viscosity also influence the system behavior. For example, although the density at point D is greater than at point C, point D extraction efficiency is slightly less. But the diffusivity is greater and the viscosity is lower for point C than for point D. Thus, the more favorable mass transport properties at condition C favor extraction when compared with conditions at point D. In the supercritical region between points B and D it appears that the magnitude of the mass transport effects are the same order or greater than the solubility effects due to density whereas at the two endpoints, A and E, the density of the extraction media, NH_3 , dominates the extraction process.

It is evident from our data that extraction in the high temperature liquid phase is more efficient in terms of solute extracted than at any of the supercritical conditions tested. However, supercritical conditions at much higher pressures may produce better extraction efficiency than in the liquid state as the supercritical fluid approaches near liquid density while maintaining more favorable transport properties.

Equipment Design Improvements

Because of the absence of reported prior art on the design of a supercritical ammonia extractor unit, several shortcomings of our equipment design became evident through use experience. These problems and suggested improvements are discussed below. These design improvements may be useful to others interested in building a supercritical ammonia extractor for future investigations.

One troublesome problem was the frequent development of ammonia leaks in the pump caused by small scratches in the sapphire plunger of the pump. The scoring of the plunger was caused by small carbon particles in the NH_3 stream released when the carbon-filled teflon O-ring degraded. The leaks were prevented by replacing the old seals with polypropylene O-rings without filler.

We found that the polypropylene O-rings were considerably more resistant to attack by ammonia than those comprised of teflon with a carbon filler. Because of the high pressure difference between the high and low sides of the pump, even minute scores in the pump plunger cause significant ammonia leaks. It therefore becomes imperative that the ammonia feed be free of particulates; ultra-pure ammonia feed stock must be used, an adequate filter to remove the fine particles must be provided, and all O-ring seals should contain no solid filler material.

Cavitation also occurred in the pump because the intake pressure was not high enough to continuously feed liquid ammonia to the pump. We used a heat gun as a stop gap measure to warm the ammonia feed reservoir to increase the intake pressure. A controlled heater should be added to the system to heat the reservoir. In addition, the intake pressure and temperature should be monitored.

The original design, based on a modified supercritical CO₂ extractor, provided a larger than necessary extractor vessel volume. This was done because most SC fluid applications involve extraction of a small amount of matter from a large volume of material, as is the case with the removal of caffeine from coffee beans. Our requirements are the opposite; we are extracting a large proportion of soluble compound from a comparatively limited volume of material. For our use, a smaller extractor vessel volume would be advantageous. Also, the separator should be located immediately after the extraction vessel, the tubing lengths could be reduced and some valves eliminated by providing upflow only through the extractor. These changes would allow for a more compact system with shorter connecting tubing lengths between extraction and separator vessels and fewer valves thereby minimizing clogging and material losses due to deposition of solute in the tubing. To prevent plugging of the expansion valve due to extremely soluble species, the solutions could be diluted with pure ammonia which is at the solution temperature and pressure at the outlet of the extractor vessel.

Automated temperature, pressure, and flow feedback control systems would aid in maintaining steady state conditions. In addition, the heating tapes currently in use should be replaced by placing the system in an automatically controlled oven to provide a constant heat source. This would maintain a more constant temperature over the system.

Finally, solutions of ammonium halides in ammonia are corrosive because they behave as strong acids. Corrosion of the stainless steel screens used to hold the sample in the extractor was evident. We suggest that the screens be made of a corrosion resistant material.

CONCLUSIONS

The solubility of ammonium chloride in SC ammonia appears to be largely a function of solvent density as shown by the increased extraction efficiency at higher SC ammonia pressure rather than being temperature dependent. In fact, maximum extraction capability was obtained using high temperature (50 °C) liquid ammonia. The higher the solvent density the greater the solvent activity in terms of solvent molecules per unit volume. Thus, a high solvent density allows greater interaction between the ionic solute and solvent molecules,

causing increased solubility. We could assume that the solubility of most inorganic compounds would go up as the SC ammonia pressure is increased. Unfortunately, our bomb and extraction systems were pressure limited to under 5000 psig. It is possible that at considerably higher SC ammonia pressure, nitrides, and especially inorganic amides and imides would be more soluble. In our studies, Si_3N_4 , AlN , BN , and $\text{Si}(\text{NH})_2$ were found to be insoluble in SC ammonia. At such high SC ammonia pressures, reactions of nitrides with the strong base NaNH_2 to form soluble complexes may also take place much in the same manner as the formation of soluble species from SiO_2 and NaOH occurs in supercritical water.

Concerning the extraction of the ammonium salt formed as a reaction product from the ammonolysis of the corresponding silicon species, SC ammonia at a higher pressure would probably afford a better separation than we found at 4000 psig. The only highly effective separation that we report with SC ammonia was the extraction of NH_4SCN from $\text{Si}(\text{NH})_2$ formed by reaction of $\text{Si}(\text{SCN})_4$ with ammonia. Probably this could have been accomplished just as well with liquid ammonia. We believe that $\text{Si}(\text{NH})_2$ is the best precursor for the production of high purity, finely divided, easily sinterable Si_3N_4 . Based on our results one of the best routes to the synthesis of pure $\text{Si}(\text{NH})_2$ is via the ammonolysis of $\text{Si}(\text{SCN})_4$ dissolved in an organic solvent. Compared to other silicon starting materials, namely the tetrahalides, the byproduct, NH_4SCN is more efficiently removed by SC ammonia and probably liquid ammonia extraction than the reaction byproducts from the ammonolysis of SiCl_4 and SiBr_4 , which are NH_4Cl and NH_4Br , respectively.

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TABLE I. - COMPOSITIONS AND BYPRODUCT REMOVAL IN Si(NH)₂ SYSTEMS

System	Initial composition		Final composition		Halides removed, percent
	Normalized, mol %	Molar ratio, X/Si	Normalized, mol %	Molar ratio, X/Si	
Si(NH) ₂ +NH ₄ Cl	Si(NH) ₂ 19.1 NH ₄ Cl 80.9	4	78.9 21.1	0.246	93.2
Si(NH) ₂ +NH ₄ SCN	Si(NH) ₂ 84.4 NH ₄ SCN 15.6	.185	100 0	0	100
Si(NH) ₂ +NH ₄ Br	Si(NH) ₂ 19.8 NH ₄ Br 80.2	4	69.4 30.6	.44	89

TABLE II. - AMMONIA USAGE

System	Steady state		Removal efficiency, percent	
	Time, hr	NH ₃ , g	NH ₄ salt (g)	
			NH ₃ (g)	Percent halide removal per gram of HN ₃
Si(NH) ₂ +NH ₄ Cl	6	600	3.856×10 ⁻³	0.155
Si(NH) ₂ +NH ₄ SCN	4-1/3	250	2.82	.40
Si(NH) ₂ +NH ₄ Br	6	555	16.69	.16

TABLE III. - SUPERCRITICAL AMMONIA EXTRACTION
 [NH₄Cl in Al₂O₃ pellets.]

	Run number ^a				
	E-1	E-2	E-3b	E-4	E-5
Experimental conditions					
Total NH ₃ flow, ACF ^b	17.05	16.38	17.06	17.04	15.32
Pressure, psi	4000	2000	5500	4000	4000
Temperature, °C	145	145	145	50	180
Weight of pellets, g					
Before extraction	17.5882	17.2687	17.4014	17.4378	17.2267
After extraction	15.9753	16.2922	15.8643	15.8975	16.2555
Weight of NH ₄ Cl, g					
Extracted	1.629	0.9765	1.5371	1.5403	0.9712
Unextracted	0.7279	0.9002	0.7430	0.1412	0.5487
Total	2.3408	1.8767	2.2801	1.6815	1.5199
NH ₄ Cl extracted, percent	68.9	52.0	67.4	91.6	63.9
NH ₄ Cl in separator, g	1.2069	0.0072	0.7184	1.9149	0.0186
NH ₄ Cl/gram of pellets	0.1331	0.1087	0.1310	0.0964	0.0882
Overall ratio (estimated)	0.1377	0.1408	0.1408	0.1408	0.1408

^aExcept run E-1 pellets used are from the same batch.

^bIn a period of 2-1/2 hr.

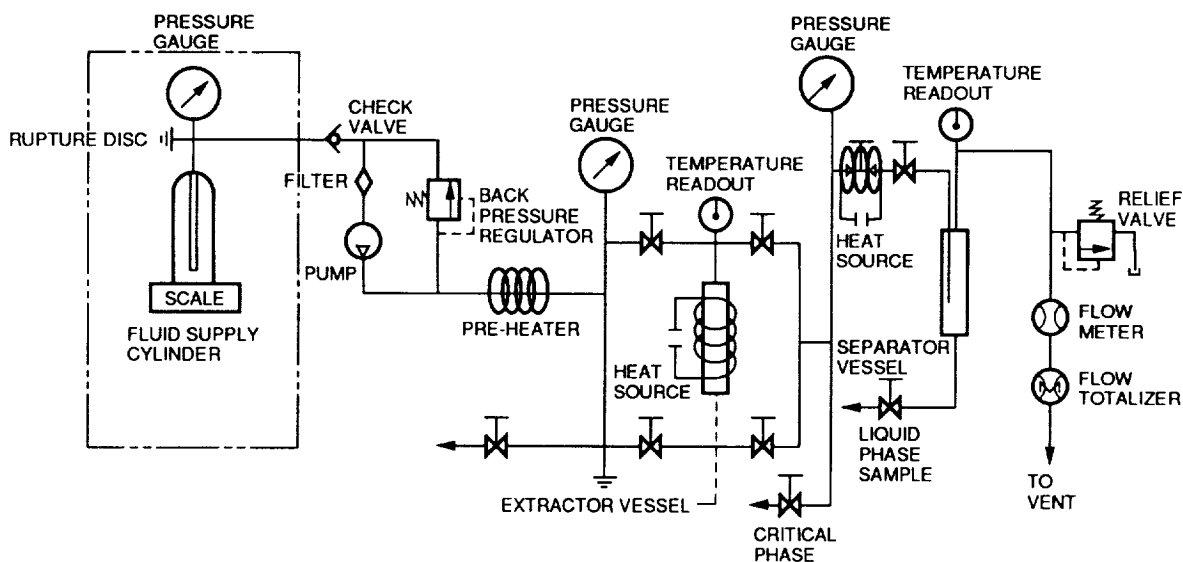


Figure 1. - Supercritical ammonia extraction unit.

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(a) Before.

(b) After.

Figure 2. - AlN powder before and after exposure to supercritical ammonia.

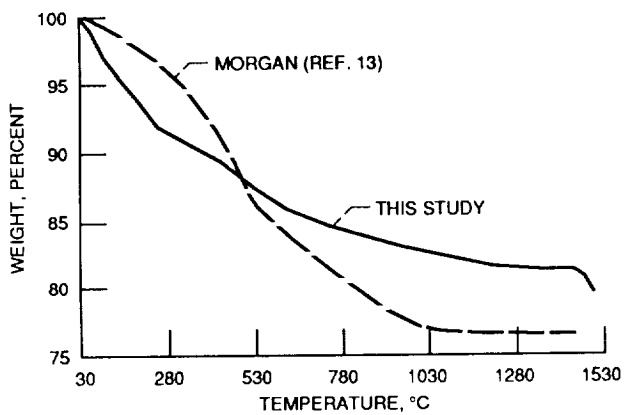


Figure 3. - $\text{Si}(\text{NH})_2$ from $\text{Si}(\text{SCN})_4$.

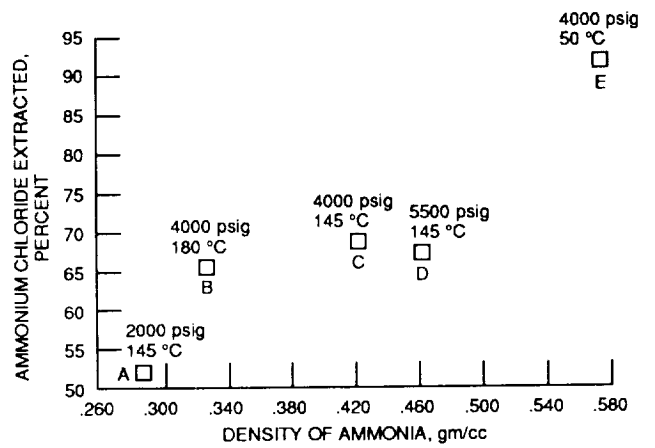


Figure 4. - Supercritical ammonia extraction; ammonium chloride in alumina beads.

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16. Abstract The extractability of ammonium halides (including ammonium thiocyanate) formed as byproducts from the synthesis of $\text{Si}(\text{NH})_2$ via ammonolysis of the corresponding silicon tetrahalides using supercritical NH_3 as the extraction medium has been investigated. It was found that the NH_4SCN byproduct of ammonolysis of $\text{Si}(\text{SCN})_4$ can be almost completely extracted with SC ammonia from the insoluble $\text{Si}(\text{NH})_2$ forming a promising system for the synthesis of pure $\text{Si}(\text{NH})_2$, one of the best precursors to Si_3N_4 . In addition, it was found that Si_3N_4 , AlN , BN , and $\text{Si}(\text{NH})_2$ are insoluble in SC ammonia. Also discussed are design considerations for a supercritical ammonia extraction unit.					
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