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LIQUID-PHASE-SINTERING PHENOMENA OF NON-OXIDE SILICON COMPOUNDS

TECHNICAL PROGRESS REPORT
For the period 01 July 1979 - 29 February 1980

D. R. Clarke
Program Manager

and

F. F. Lange
Co-Principal Investigator

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Thousand Oaks, CA 91360

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Prepared for

**Department of Energy
Division of Material Science**

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1.0 INTRODUCTION

This report describes the technical progress made to date in the second year of an investigation into the phenomena associated with liquid phase sintering of silicon nitride alloys.

The principal effort in the first six months has been to determine the elemental composition of the non-crystalline intergranular phase in a series of silicon nitride alloys sintered with MgO. The rationale of the work being to ascertain the composition of the liquid phase present during sintering of these alloys. The work is summarized in the following section and described in the accompanying papers being submitted for publication (Appendices 1 & 2). One of the findings of this work was that the solidified liquid phase had a composition close to the SiO_2 - MgSiO_3 tie line. This contrasted with the fact that the crystalline phases present demonstrated that the alloys had the expected composition within the Si_3N_4 - $\text{Si}_2\text{N}_2\text{O}$ - Mg_2SiO_4 compatibility triangle; the intergranular phase composition lay outside this triangle. It was also found that the intergranular phase exhibited both compositional and morphological evidence characteristic of phase separation having occurred. As a miscibility gap is known to exist between SiO_2 and MgSiO_3 it was concluded by analogy that the intergranular phase can decompose by phase separation under appropriate conditions. On the basis of this conclusion and the fact that phase separation within a miscibility gap is often a preliminary stage in the crystallization of glass ceramics an attempt was made to crystallize the intergranular phase of a silicon nitride alloy

using a nucleating agent. Platinum was chosen as it is known not to react with silicon nitride and has been used to nucleate other glass ceramics successfully. The platinum was added as platinum chloride. The experiments have been unsuccessful to date because full density could not be obtained and as is described in Section 2 this is attributed to the presence of chlorine within the alloy. However, this work has demonstrated the retardent effect of chlorine impurities on the densification of silicon nitride alloys. As a result some effort was expended on testing available silicon nitride powders for the presence of chlorine impurities.

Work also in progress has been directed to using a transient eutectic phase to liquid phase sinter silicon nitride alloys in the Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ - $\text{Si}_2\text{N}_2\text{O}$ phase compatability triangle. The objective is to use a eutectic liquid whose composition lies outside the Si_3N_4 - $\text{Y}_2\text{Si}_2\text{O}_7$ - $\text{Si}_2\text{N}_2\text{O}$ phase field but has a comparatively lower melting temperature to densify silicon nitride powders. Only sufficient eutectic liquid (added as a glass) is mixed with the silicon nitride grains to keep the overall composition within the required phase field, thus the idea is that the eutectic liquid is only present as an intermediary phase prior to attaining equilibrium. The advantage of this approach is expected to be that densification occurs at a lower temperature than if the eutectic in the required phase field were used thereby minimising the temperature dependent volatilization processes competing with densification. As described in Section 2.4 the eutectic required has been fabricated as a glass and a number of sintering runs have been performed but it is still too early to determine whether the approach is as promising as it appears in theory.

2.0 PROGRESS DURING CURRENT PERIOD.

In the following sub-sections the progress made during the second year of the program is described.

2.1 Elemental Composition of the Intergranular Phase

In the past four years extensive electron microscopical investigations⁽¹⁻⁷⁾ have been performed that demonstrated beyond doubt the existence of a continuous intergranular phase in a variety of silicon nitride based alloys. The thickness of the intergranular phase appears to vary from one alloy to another (for instance 8-20Å in MgO fluxed Si_3N_4 ⁽¹⁻⁵⁾ to 20-75Å in magnesium sialons⁽⁶⁾) with the bulk of the phase located at three and four grain junctions. Recent convergent beam electron diffraction investigations⁽³⁾ have shown that pockets of the intergranular phase are non-crystalline and although the intergranular phase at two grain junctions is too narrow to investigate it is assumed to be non-crystalline also. Despite these advances little work has been directed toward determining the elemental composition of the intergranular phase. It is important to know the composition of the phase since its properties (viscosity, diffusivity) appear to control the elevated temperature properties (e.g. oxidation resistance,⁽⁸⁻¹⁰⁾ creep,⁽¹²⁾ strength⁽¹³⁾ and failure mechanisms⁽¹⁴⁾) of silicon nitride alloys. It is also important to know as it is most probably the liquid phase present during sintering and as such plays an important role in the various processes occurring during sintering. According to the rules of phase equilibria

the last liquid to solidify out of a melt on cooling at equilibrium - whether as a crystalline or non-crystalline solid - will have the composition corresponding to the eutectic composition. For this reason it is expected that the intergranular phase should have the same composition as the ternary eutectic phase. Some Auger electron spectroscopy investigations^(15,16) have been carried out on intergranular fracture surfaces of silicon nitride alloys to determine the composition of the intergranular phase but in view of the extreme thinness of the phase and the lack of spatial resolution of the technique as implemented there persists some uncertainty as to the microstructural origin of the Auger signal. For these reasons it was felt necessary to determine the elemental composition of the intergranular phase.

On account of the extremely fine scale of the intergranular phase the transmission electron microscopy techniques of x-ray microanalysis and electron energy loss spectroscopy have been utilized in the current program to determine the elemental composition. The x-ray microanalysis was performed at the Science Center and the Electron energy loss spectroscopy was carried out on the same samples at Oak Ridge National Laboratory in collaboration with Drs. N.J. Zaluzec and R. W. Carpenter.

Details of the microanalysis experiments and the findings we described in the two manuscripts comprising the appendices. Two different alloy compositions in the Si_3N_4 - $\text{Si}_2\text{N}_2\text{O}$ - Mg_2SiO_4 phase compatibility triangle were investigated; an alloy containing 75 m/o Si_3N_4 (similar to commercially available alloys) and an alloy having a composition corresponding to the ternary eutectic previously determined by Lange.⁽¹⁷⁾ The latter alloy was

examined in two states, as fabricated and subsequently after heating above the eutectic temperature and rapidly cooling to increase the volume fraction of the glass in the microstructure. Common to all three alloys were the findings that the intergranular phase was non-crystalline and had a composition close to the $\text{SiO}_2\text{-MgSiO}_3$ tie line. No nitrogen was detected in the intergranular phase implying that its concentration was below the detectability limit of the electron energy loss spectroscopy technique as applied to that particular material. The presence of small crystallites of $\text{Si}_2\text{N}_2\text{O}$ in the intergranular phase suggests that it did at one time contain nitrogen. The fact that the microanalysis results place the composition near the $\text{SiO}_2\text{-MgSiO}_3$ tie line means that the intergranular phase does not have the composition of the ternary eutectic and suggests that it is a non-equilibrium intermediate phase. This was despite the fact that the crystalline phases present were these expected from the compatibility triangle. As yet phase equilibrium studies are insufficiently advanced for the formation of such an intermediary composition to be explained on the basis of the phase equilibrium diagram. However, the formation of a highly siliceous liquid phase during sintering has important implications for the kinetics of densification. Another finding that attests to the fact that full equilibrium is not attained is the non-uniform distribution of impurities within the glassy phase. The principal impurities detected were Cl, Ca, Al and Na, the latter three expected to lower the eutectic and glass transition temperatures of the intergranular phase.

Another finding of considerable interest was the observation of characteristic features of phase separation within the intergranular phase. Specifically light, globular non-crystalline regions having a composition close to SiO_2 were present within a darker, non-crystalline matrix whose composition was closer to MgSiO_3 and also contained the impurities Ca and Al. Such phase separation is consistent with the composition lying between SiO_2 and MgSiO_3 where a miscibility gap is known to exist.⁽¹⁸⁾ The evidence of possible phase separation and the existence of the miscibility gap led to attempts to crystallize the intergranular phase described in the following sub-section.

2.2 Crystallization of the Intergranular Phase

It has been proposed that one method of improving the elevated temperature properties of silicon nitride alloys is to crystallize the glassy intergranular phase. Although the eutectic melting temperature would be unaffected the strength and rigidity of the material would not decrease as rapidly with temperature as they appear to above a glass transition temperature of the non-crystalline intergranular phase. The observation of elemental and morphological evidence consistent with the intergranular phase having undergone phase separation during fabrication and cooling suggests that nucleated crystallization of the intergranular phase might be feasible. The basis of this being that phase separation in a glass is believed to be an intermediate step in the devitrification of glass ceramics. Furthermore the observation (see appendix) of small crystallinities of both $\text{Si}_2\text{N}_2\text{O}$ and MgSiO_3

surrounded by glass suggests that they may have crystallized from the intergranular phase without a nucleating aid.

To test whether the intergranular phase in a silicon nitride alloy densified with MgO could be crystallized a series of experiments were carried out using a nucleating agent to aid crystallization. Of the common nucleating aids used in glass ceramics, TiO_2 and ZrO_2 are unsuitable as they are known to react chemically with Si_3N_4 . For this reason platinum was chosen. It is also a general purpose nucleating aid. In order to form a fine dispersion of platinum the standard practice of adding platinum to the ceramic powder in the form of platinum chloride was adopted; the platinum being formed by thermal decomposition. In the experiments two batches of powder were mixed, one having a composition of 0.75 m/o Si_3N_4 + 0.09 m/o SiO_2 + 0.16 m/o MgO and the other being identical but for the addition of 5 w/o of the platinum salt. The material without the platinum addition being a control sample. The two powders were then hot-pressed together in the same die (but separated by a sheet of grafoil) at 1750°C for two hours followed by a thermal hold at 1000°C for four hours. The intermediate temperature hold being for the purpose of nucleation and growth of crystallinities in the intergranular phase. After hot pressing the control sample has a density of 91.8% of theoretical whereas the sample incorporating the nucleating agent had a density of only 86.8%, both considerably lower than the theoretical density known from previous experience to be achievable with the sample composition under the same hot-pressing conditions. Another notable feature of the samples was that after cutting they were seen to be hygroscopic. On drying the samples a white residue

remained that had a sharp taste and by energy dispersive x-ray analysis consisted primarily of chlorine (Fig. 1). The substance gave rise to a crystalline X-ray diffraction pattern which is quite reproducible after cycling between wet and dry atmospheres. The substance has yet to be positively identified and at the present time is believed to be an intimate mixture of at least two compounds. As only chlorine has been detected by EDAX the substance must also contain elements having an atomic number of less than twelve such as nitrogen, hydrogen and carbon. Compounds such as ammonium chloride formed by the reactions of chlorine with ammonia produced by the hydrolysis of the silicon nitride are thought to be likely constituents of the substance.

Further attempts to crystallize the intergranular phase whilst maintaining full densification are in progress using other known nucleating agents to determine whether the observed phase separation in the intergranular phase can be utilized.

It would appear from the findings that the chlorine produced by the decomposition of the platinum chloride salt retarded densification in the silicon nitride alloys both in the one containing the chloride and the one physically separated from it by the grafoil disc. As such it is a vivid demonstration of the effect that chlorine impurities can have on densification. For this reason a number of silicon nitride powders have been analysed to determine whether they contain chlorine impurities.

Fig. 1 EDAX spectrum obtained from the white residue formed on exposing the silicon nitride alloy containing platinum chloride to air. The spectrum indicates that the principal element present is chlorine.

2.3 Impurities Analysis of Silicon Nitride Powders

This is important not only because of the detrimental effect chlorine has on densification but because a number of the available silicon nitride powders are produced by the decomposition of chlorine containing gases, e.g., by the reaction of silicon tetrachloride and ammonia

The level of chlorine impurities in the silicon nitride powders is low since it cannot normally be detected by EDAX in the scanning electron microscope. for this reason a wet chemical method was adopted. The method consists of boiling the powder with distilled water, filtering and testing the distillate with a silver nitrate solution in dilute nitric acid. If chlorine is present an opalescent white precipitate is formed which is soluble in ammonia. The method is extremely sensitive to the presence of chlorine. The results of the test are presented in Table I. Whilst the chlorine level is expected to vary from one manufacturing batch to another, the above test can be used quite quickly to determine whether chlorine is present. For future work in the program only silicon nitride powders that give no discerable precipatate will be used.

Another aspect of the impurity content of silicon nitride powders is evident on viewing various silicon nitride powders side by side; they are all colored to various degrees. Pure silicon nitride such as whiskers grown from the vapour are transparent (white when finely divided). The coloration of the

TABLE 1

Si ₃ N ₄ Powder	Test Reaction
Amorphous GTE	Thick White Precipitate
α - GTE - 502	Slight precipitate
KBI	No precipitate
Cerac - β - 1481	No precipitate
*Cabosil (SiO ₂)	No precipitate
*MgO	No precipitate

*For comparison purposes.

commercial powders is widely believed to be due to the presence of unreacted silicon. However this cannot entirely be the case since it has been found that the powder fluoresce in different colors when viewed in ultra-violet light. In order to identify the impurities responsible for the observed fluorescence the available powders are being analysed by fluorescence optical spectroscopy. Surprisingly such analysis does not appear to have been performed previously. The interest of this work is not the identification of impurities per-se but rather finding the purest silicon nitride powders for studying the densification of silicon nitride powders whilst minimizing interference from impurities.

2.4 Transient Eutectic Densification

Following the demonstration⁽¹⁹⁾ that the presence of a liquid phase is necessary for densification of silicon nitride powders it was proposed to use a transient eutectic phase to sinter silicon nitride alloys. In essence the idea is to lower the temperature (thereby reducing the temperature dependent volatilization losses) of sintering by using the lowest melting temperature eutectic in the phase diagram. For the reasons given in the introduction the $\text{Si}_3\text{N}_4 - \text{SiO}_2 - \text{Y}_2\text{O}_3$ system was chosen for study, and compositions in the $\text{Si}_3\text{N}_4 - \text{Si}_2\text{N}_2\text{O} - \text{Y}_2\text{Si}_2\text{O}_7$ chosen for fabrication. In the $\text{Si}_3\text{N}_4 - \text{SiO}_2 - \text{Y}_2\text{O}_3$ system the lowest melting eutectic reported⁽²⁰⁾ lies in the $\text{SiO}_2 - \text{Si}_2\text{N}_2\text{O} - \text{Y}_2\text{Si}_2\text{O}_7$ phase field and melts at $\sim 1550^\circ\text{C}$ (E1 in Fig. 2). To fabricate a material having a composition such as B (Fig. 2) using the eutectic composition it is necessary to mix the eutectic with silicon nitride powder in amounts according to the lever rule; no other additives are necessary. On heating the two together above the eutectic temperature the eutectic compound melts, providing a liquid phase (for densification by solution - reprecipitation of the silicon nitride), which is then consumed by reaction with the silicon nitride to form the secondary phases in the $\text{Si}_3\text{N}_4 - \text{Si}_2\text{N}_2\text{O} - \text{Y}_2\text{Si}_2\text{O}_7$ phase compatibility triangle.

A prerequisite for this process is the formation of the eutectic compound as a homogeneous phase such as a glass. After considerable experimentation the ternary eutectic composition has been produced in a form that is almost entirely non-crystalline. Mixtures of Si_3N_4 , SiO_2 and Y_2O_3 powders have been heated in molybdenum crucibles under an atmosphere of nitrogen and

Fig. 2 Si₃N₄-SiO₂-Y₂O₃ behavior diagram indicating the composition of the Si₂N₂O-SiO₂-Y₂Si₂O₇ ternary eutectic (E₁) and the SiO₂-Y₂Si₂O₇ binary eutectic (E₃) together with the alloys A and B being fabricated using these eutectics.

then cooled. In this way translucent glassy bodies could be formed with only a very fine dispersion ($\sim 300 \text{ \AA}$) of crystallites present. A typical region is shown in the transmission electron micrograph of Fig. 3 together with the selected area diffraction pattern obtained from the same region. At present it is not known whether the material corresponds to the eutectic composition or whether some loss of nitrogen (by thermal decomposition of the silicon nitride) may have occurred during preparation of the eutectic. An alternative strategy presently being investigated is to fabricate the binary eutectic existing between SiO_2 and $\text{Y}_2\text{Si}_2\text{O}_7$ (40 w/o SiO_2 + 60 w/o Y_2O_3 , at 1660°C) as a glass for use as the transient eutectic. This has the intrinsic advantage of not being susceptible to compositional change during preparation due to loss of nitrogen as is the case with the ternary eutectic. So far it has not proved possible to form as a glass although the work is continuing.

Having obtained the eutectic as a glass the next step is to crush it to form a powder and then intimately mix with silicon nitride powder (in proportions dictated by the lever rule). Finally, the composite powder is heated to the densification temperature just above the appropriate eutectic temperature. This procedure has been followed and whilst the experiments are still at an early stage it is apparent that densification does occur using the transient eutectic. In the following months densification kinetics and phase transformation kinetics will be measured as a function of sintering temperature and compared with those measured for the same alloy produced from Si_3N_4 , SiO_2 and Y_2O_3 starting powders.

Fig. 3 TEM bright field micrograph of the ternary eutectic (E_1) showing small crystallites embedded in a predominately non-crystalline matrix. The lower illustration is of the diffraction pattern obtained from the matrix indicating it to be non-crystalline.

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LIST OF PUBLICATIONS RESULTING FROM DOE SUPPORT

1. "Volatilization Associated With the Sintering of Silicon Nitride Compositions," F. F. Lange, Journal of the American Ceramic Society. Submitted.
2. "Thermal Etching and Grain Boundary Grooving of Silicon Ceramics," W. Robertson, Journal of the American Ceramic Society. Submitted.
3. "Densification of Silicon Nitride Alloys Using a Eutectic Liquid: An Experimental Test," D. R. Clarke, Proc. 5th International Conference on Sintering and Related Phenomena. Edited G. Kuczynski. In press (Plenum press).
4. "Liquid Phase Sintering: Are Liquids Squeezed Out From Between Compressed Particles?" F. F. Lange, Journal of the American Ceramic Society. Submitted.
5. "Silicon Nitride Alloy Systems: Fabrication, Microstructure and Properties," F. F. Lange, International Metallurgical Reviews, In press.
6. "The Intergranular Phase in Hot-Pressed Silicon Nitride Alloys. I. Elemental Composition." D. R. Clarke, N. J. Zaluzec and R. W. Carpenter, Journal of the American Ceramic Society. Submitted.
7. "The Intergranular Phase In Hot-Pressed Silicon Nitride Alloys. II. Evidence for Phase Separation and Crystallization." D. R. Clarke, N. J. Zaluzec and R. W. Carpenter, Journal of the American Ceramic Society. Submitted.

APPENDIX 1.

THE INTERGRANULAR PHASE IN HOT-PRESSED SILICON
NITRIDE ALLOYS. I. ELEMENTAL COMPOSITION

(Submitted to the Journal of the American Ceramic Society)

THE INTERGRANULAR PHASE IN HOT-PRESSED SILICON NITRIDE ALLOYS
I. ELEMENTAL COMPOSITION

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ABSTRACT

The elemental composition of the noncrystalline intergranular phase in three MgO fluxed hot-pressed silicon nitride alloys, determined by x-ray microanalysis and electron energy loss spectroscopy in the transmission electron microscope, is reported. The composition is similar in all three alloys and lies close to the $\text{SiO}_2\text{-MgSiO}_3$ tie line with impurities of Ca, Al, and Cl. No nitrogen in the noncrystalline phase could be detected implying that the nitrogen concentration was below the experimental detectability limit.

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I. INTRODUCTION

The high temperature strength,^{1,2} fracture mechanisms,²⁻⁴ compressional creep⁵⁻⁹ and oxidation resistance¹⁰⁻¹³ of a variety of silicon nitride alloys hot-pressed with magnesia are controlled by the intergranular phase present in these alloys. Since in each case the properties are inferior to those expected of pure, single-phase silicon nitride, as exemplified for instance by those of CVD silicon nitride, it can be concluded that they must be largely determined by the properties of the intergranular phase. Yet despite the widespread recognition of the role played by the intergranular phase, little is known about its properties except for a value of its viscosity deduced from elevated temperature internal friction measurements of silicon nitride billets.¹⁴ In order to proceed in fabricating quantities of the intergranular phase material for measurements of its high temperature properties it is essential to know its chemical composition.

Two approaches that have been adopted are evident. The first is the direct compositional analysis of the intergranular phase in hot-pressed material and some limited data has been obtained in this manner by Auger electron spectroscopy¹⁵⁻¹⁷ of intergranular regions exposed by room temperature fracture. The second approach has been by phase equilibria studies. According to the rules of phase equilibria the last liquid to solidify out of a melt at equilibrium - whether as a crystalline or noncrystalline solid - will have the composition corresponding to the eutectic composition. On the basis that the intergranular phase is the last material to solidify, a number of phase equi-

libria studies have been performed to identify the eutectic compositions of silicon nitride alloys.¹⁸

The objective of the work described in the present paper was to combine the two approaches by determining the elemental composition of the intergranular phase in a hot-pressed silicon nitride alloy and comparing it to the composition of the appropriate eutectic. As the technique of Auger electron spectroscopy (as presently implemented on existing instruments) lacks the spatial resolution necessary, the complementary transmission electron microscopy techniques of x-ray energy dispersive spectroscopy (EDS)¹⁹⁻²¹ and electron energy loss spectroscopy (EELS)^{19,22} have been used as the principal analytical methods for determining the elemental composition of the intergranular phase.

II. EXPERIMENTAL PROCEDURE

1. Sample Compositions

Alloy compositions from within the Si_3N_4 - $\text{Si}_2\text{N}_2\text{O}$ - Mg_2SiO_4 phase compatibility triangle of the Si_3N_4 - SiO_2 - MgO system were chosen for examination since the behavior diagram is substantially agreed upon by various investigators^{1,23,24} and previous phase equilibria work by Lange¹⁸ has established the binary and ternary eutectics in the compatibility triangle. The ternary eutectic is reported to be at a composition of 0.10 Si_3N_4 + 0.30 $\text{Si}_2\text{N}_2\text{O}$ + 0.60 Mg_2SiO_4 and to become a liquid at 1515°C. Binary eutectics are also reported at 0.39 $\text{Si}_2\text{N}_2\text{O}$ + 0.61 Mg_2SiO_4 between $\text{Si}_2\text{N}_2\text{O}$ and Mg_2SiO_4 and at 0.19 Si_3N_4 + 6.81 Mg_2SiO_4 between Si_3N_4 and Mg_2SiO_4 . In addition, substitution of Ca for Mg in the ternary eutectic composition lowers its melting temperature to a minimum of 1325°C at 60% substitution. In the present study three alloys were examined in detail, the ternary eutectic composition (A), the binary eutectic between $\text{Si}_2\text{N}_2\text{O}$ and Mg_2SiO_4 (B) and a sample consisting primarily of Si_3N_4 (C) having a composition 0.75 Si_3N_4 + 0.09 SiO_2 + 0.16 MgO . The binary eutectic alloy was chosen primarily as a calibration standard for the electron energy loss spectroscopy investigations, and the ternary eutectic to ensure that the microstructure contained a relatively large volume fraction of the intergranular phase.

2. Sample Preparation

The alloys were prepared by hot-pressing composite powders of Si_3N_4 , SiO_2 and MgO in a grafoil lined graphite die at 28 MPa. Relatively pure, high

alpha phase Si_3N_4 ($\alpha/\beta = 9$) powder was used in making the composite powder, which was mixed and milled prior to hot-pressing. The alloys A, B and C were hot-pressed at temperatures of 1500°C, 1500°C and 1750°C, respectively for two hours. Subsequent x-ray diffraction of the as-fabricated materials showed a total conversion of α - to β - Si_3N_4 and no indication of remanant SiO_2 or MgO .

Samples for transmission electron microscopy were prepared by diamond cutting of thin slices, grinding and polishing to form ~50 μm thick discs and subsequent ion-thinning. They were then coated with a thin layer (~10 nm) of evaporated carbon (to suppress surface charging) prior to analysis in the microscope.

3. Microanalysis Techniques

The fine-scale (<100 nm) of the intergranular phase in hot-pressed silicon nitride alloys required the microanalysis to be performed using the transmission electron microscope. In fact, two transmission microscopes were used, one (Philips EM400) fitted with an energy dispersive x-ray spectrometer and the other (JEOL 100CX) fitted with an electron energy loss spectrometer, designed by one of the authors (NJZ). The x-ray microanalysis technique in the transmission electron microscope has been described sufficiently in print¹⁹⁻²¹ not to warrant further description here. The technique of electron energy loss spectroscopy (EELS) is less well known, being still in the development stage.

The electron energy loss studies reported here were performed on a $\pi/2$ magnetic sector electron energy analyzer designed and built at

ORNL.^{25,26} During this series of experiments the energy resolution of the experimental apparatus was chosen to be 20 eV at an acceptance angle to the spectrometer of ~ 15 mr. Spectra were recorded over the energy loss range 0-25 keV with typical acquisition times being from 100 to 300 sec per 1024 channel spectrum. This energy range was sufficient to detect K shell ionization losses from the elements in the range $3 < Z < 15$ and L shell losses for $13 < Z < 40$ providing adequate overlap between EELS and subsequent EDS measurements.

The incident electron beam energy during all measurements in this study was 120 keV and a nominal electron probe diameter of 40 nm was used throughout. Care was also taken to operate at specimen thickness such that multiple inelastic scattering events were not substantial²⁷ and under diffracting conditions to minimize anomalous effects due to the orientation dependence of inelastic scattering.^{28,29} The specimen thickness greatly affects the quality of the electron energy loss spectra; increasing thickness broadens the characteristic energy loss peaks and reduces their peak to background ratios hence decreasing the minimum detectable concentration. Generally, regions thin enough so that the ratio of the first plasmon peak to zero-loss peak heights was smaller than 0.25 were sought. Quantitative analysis was performed using a series of operator interactive Fortran computer programs written at ORNL³⁰ based on the formalism outlined by Egerton.²⁸ In order to eliminate the detrimental accumulation of contamination during EELS measurements all spectra were recorded with the specimens at liquid nitrogen temperatures. This precaution enabled regions of interest to be studied for several hours without significant contamination.

III. OBSERVATIONS

All three of the alloys examined by transmission microscopy were found to contain an intergranular noncrystalline* phase with the ternary eutectic alloy (A) having the largest volume fraction as expected. Three techniques were used to determine that the intergranular phase was noncrystalline: (1) convergent beam electron diffraction patterns of pockets of the phase (>20 nm in size) showing characteristic diffuse diffraction halos; (2) dark field imaging^{31,32} using the diffuse ring of scattered electrons located at approximately 0.34 nm^{-1} in reciprocal space showing a continuous intergranular film between the crystalline grains; and (3) diffraction contrast experiments where upon tilting the specimens with respect to the electron beam the intergranular pockets did not alter their contrast.

The microstructure of the ternary eutectic alloy consisted of three crystalline phases and a noncrystalline intergranular phase located principally at three and four-grain junctions. The three crystalline phases, distinguishable by their distinct and characteristic electron energy loss spectra, were found to be silicon nitride (Si_3N_4), silicon oxy-nitride ($\text{Si}_2\text{N}_2\text{O}$) and forsterite (Mg_2SiO_4) in agreement with the alloy being in the phase compatibility triangle formed by these three terminal phases. Relatively

*The general term noncrystalline is used here rather than the explicit terms glassy or amorphous since there is as yet no information available as to whether the intergranular phase undergoes a first or second order change on cooling.

large pockets of intergranular phase, sufficiently large for microanalysis without interference from adjacent grains, were observed throughout the microstructure as illustrated by the example in Fig. 1(a). As indicated by the convergent beam electron diffraction pattern of Fig. 1(b) the wedge-shaped intergranular phase is noncrystalline. The electron energy loss spectrum recorded from the same pocket is reproduced in Fig. 1(c). Only Si and O are detectable in the spectrum. Quantitative analysis of the spectrum yields a composition 40 a/o Si, 60 a/o O. Electron energy loss spectra from the adjacent grains, A and B, identifies them as being silicon oxy-nitride and forsterite (Fig. 1(d) and (e)), respectively. No nitrogen was detectable in the forsterite.

Another example of the noncrystalline phase in the ternary eutectic alloy is shown in Fig. 2(a). In this particular case the intergranular phase is located between long plate-like grains which electron energy loss spectroscopy indicate to be silicon oxy-nitride and as can be seen in Fig. 2(a) consists of both light and dark regions. The electron energy loss spectrum obtained from the dark region b of the intergranular phase is shown in the middle spectrum of Fig. 2(b). Silicon, oxygen and magnesium are present and quantitative analysis yields a composition 22 a/o Si, 7 a/o Mg, 70 a/o O. Presently unquantifiable due to insufficient cross section information but just detectable by a slight change of slope in the recorded EELS spectrum is a trace of Ca present. The spectrum from the light region a is reproduced at the bottom of Fig 2(b) showing only Si and O.

As the x-ray microanalysis was performed separately after scrutiny of the microscope plates recorded as part of the electron energy loss spectroscopy investigations it was possible to further analyze the two different noncrystalline regions. X-ray spectra from the light and dark regions c and d are reproduced in Fig. 2(c) and (d), respectively. Only Si is detectable in the light region whereas Si, Mg, Ca, Al and Cl are detectable in the dark region. This suggests that phase separation within the intergranular phase has occurred. This is discussed in the accompanying paper (Part II). The observation of an intergranular phase consisting of two distinct regions was well established and Fig. 2(a) is the clearest example since it was one of the largest noncrystalline regions found in the microstructure.

Alloy C, consisting principally of silicon nitride, also contained pockets of the intergranular phase but these were generally smaller in size than those in the ternary eutectic alloy. This is consistent with there being a smaller volume fraction of the phase. The overall microstructure of alloy C was similar to that previously reported for commercial silicon nitride alloys hot-pressed with similar amounts of MgO. Despite the small size of the intergranular phase pockets compared to those in alloy A some electron energy loss spectroscopy was possible as is illustrated by the micrograph and spectra of Fig. 3. Although region A is not clearly delineated in Fig. 3(a) its convergent beam electron diffraction pattern, Fig. 3(b), indicates that it is noncrystalline. The electron energy loss spectrum recorded from the same region, Fig. 3(c), shows that it consists of Si, O and Mg at a composition of 49 a/o O, 24 a/o Mg, 27 a/o Si. No nitrogen was detectable in the spectrum.

The spectrum from an adjacent noncrystalline region, B, suggested that it contained Si, O and N, but the region was too small to be sure that some of the spectrum did not originate from a neighboring silicon oxy-nitride grain. Nevertheless, the absence of any Mg peak in the spectrum suggested that the intergranular phase consisted primarily of Si and O, in which case its composition would be similar to that of the lighter regions found in alloy A.

The microstructure of the binary eutectic alloy, B, was quite different to that of either the ternary eutectic alloy, A, or the predominantly Si_3N_4 alloy, C. It consisted by and large of long plate-like grains surrounded by a uniform crystalline matrix as in the micrograph of Fig. 4. The material was not studied in great detail since it was fabricated primarily for use as a calibration check of the quantitative techniques used in analyzing the electron energy loss and x-ray spectra. Also, no large pockets of intergranular phase were found. In agreement with x-ray diffraction results, only two crystalline phases were found, silicon oxy-nitride and forsterite. The long fibers and the matrix gave x-ray spectra as shown in Fig. 4(b) and 4(c), respectively, indicating that the microstructure consisted of silicon oxy-nitride fibers in a matrix of forsterite.

IV. DISCUSSION

The principal finding based on over thirty spectra is that the composition of the intergranular noncrystalline phase corresponds to a composition in the $\text{Si}_2\text{N}_2\text{O}$ - SiO_2 - MgSiO_3 phase field rather than to the ternary eutectic in the Si_3N_4 - Mg_2SiO_4 - $\text{Si}_2\text{N}_2\text{O}$ compatibility field. Since no nitrogen was detectable in the noncrystalline phase, the composition must lie in the vicinity of the SiO_2 - MgSiO_3 tie line. This conclusion is supported by the evidence of phase separation in the intergranular phase discussed in part II. The obvious conclusion to be drawn is that the hot-pressing conditions were insufficient to fully attain equilibrium despite the x-ray diffraction finding that the crystalline phases were as expected of equilibrium, i.e., Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$ and Mg_2SiO_4 . However, the conditions used are quite typical of those used in fabricating silicon nitride alloys, implying that the majority of such alloys may also have not totally attained equilibrium. The question then arises whether the presence of a highly siliceous intergranular phase is more or less detrimental to the high temperature properties of silicon nitride alloys than one having a composition corresponding to the ternary eutectic. Only further experiments can resolve this question.

The nitrogen content in the intergranular phase remains unknown despite the use of electron energy loss spectroscopy, which is sensitive to the presence of nitrogen. This implies that the nitrogen content is below the detectability limit for the particular experimental conditions used. An independent experiment²⁵ under the same electron-optical conditions used in this

work showed that nitrogen was just detectable in a single phase nitrogen apatite, $Y_{10}(SiO_4)_6 N_2$. The nitrogen content in this phase is 4.76 a/o. As the average atomic number of $Y_{10}(SiO_4)_6 N_2$ is significantly higher than the silicon nitride alloy, the detectability limit of N in the noncrystalline phase may in the absence of peak interference effects be lower than 4.75 a/o. Since the typical specimen thickness of the areas analyzed during these experiments was near the maximum recommended for quantitative analysis²⁷ a conservative estimate of the detectability limit of N in these alloys is ~5 atomic %. For comparison, the nitrogen content of the ternary eutectic composition in the Si_3N_4 - Si_2N_2O - Mg_2SiO_4 is calculated to be ~15 a/o. It is assumed that no nitrogen loss from the intergranular phase occurs during the ion-beam thinning step of sample preparation.

The observation of Ca, Al, and Cl in the noncrystalline phase is similar to the finding of Ca and Al in the intergranular phase in a hot-pressed Mg-Si-Al-O-N polytype alloy.³³ It appears that the noncrystalline phase is capable of accommodating such impurities and existing over a range of compositions. None of these impurity elements were detectable in the crystalline phases. Their presence in the intergranular phase, particularly glass-formers such as Al and glass-modifiers such as Ca, will undoubtedly affect its properties including viscosity and softening temperature, and hence the high temperature properties of the silicon nitride alloys. The finding of Cl in the intergranular phase substantiates the suggestion proposed by Morgan³⁴ that Cl can remain in hot-pressed compacts even up to 1750°C and can also inhibit reactive hot-pressing.

V. CONCLUSIONS

The noncrystalline intergranular phase in three hot-pressed silicon nitride alloys containing MgO has been found to have a composition close to the $\text{SiO}_2\text{-Mg}_2\text{SiO}_3$ tie line. This finding of a composition removed from the ternary eutectic in the $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-Mg}_2\text{SiO}_4$ phase field suggests that phase equilibrium during hot-pressing is not totally attained despite the x-ray diffraction evidence that the bulk of the materials has reached equilibrium. The exact composition of the noncrystalline phase varies from one location to another in the microstructure and incorporates impurities including Ca, Al, and Cl. These impurities will unquestionably affect the high temperature properties of the intergranular phase. The study also demonstrates the utility of combined x-ray microanalysis and electron energy loss spectroscopy in the transmission microscope for the elemental analysis of minor phases not detectable by x-ray diffraction.

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FIGURE CAPTIONS

- Fig. 1 (a) A wedge-shaped pocket of the intergranular phase in the ternary eutectic alloy, A, together with the convergent beam electron diffraction pattern (b) indicating the phase to be noncrystalline. The electron energy loss spectra from the intergranular phase G, and the adjacent crystalline grains A and B are shown in (c) (d), and (e), respectively.
- Fig. 2 Fig. 2(a) Another example of the noncrystalline phase in the ternary eutectic alloy. Figure 2(b) are the electron energy loss spectra recorded from one of the crystalline regions A (top), the dark noncrystalline region, b, (middle) and the light region, a, at the bottom. The x-ray spectra from the dark and light regions, c and d, are reproduced in Fig. 2(c) and (d), respectively. They confirm the phase separation.
- Fig. 3 Transmission electron micrograph of the Si_3N_4 rich alloy, C. The convergent beam electron diffraction pattern (Fig. 3b) of region A shows it to be noncrystalline and its electron energy loss spectrum, (Fig. 3c) shows that it consists of Si, O and Mg. The adjacent region, B, also noncrystalline, exhibits a loss spectrum of Si and O (Fig. 3d).
- Fig. 4 (a) An example of the microstructure of the binary eutectic alloy, B, together with the x-ray spectra obtained from adjacent grains indicating that it consists of fibers or plates of $\text{Si}_2\text{N}_2\text{O}$ (b) in a matrix of Mg_2SiO_4 (c).

Figure 1(a)

Figure 1(b)

Figure 1(c),(d),(e)

Figure 2(a)

SC5178.3TR

Figure 2(b)

SC5178.37TR

Figure 2(c),(d)

Figure 3(a)

Figure 3(b)

Figure 3(c),(d)

Figure 4(a)

Figure 4(b),(c)

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