NASA Technical Paper 1382

Effect of Oxygen-Nitrogen Ratio on Sinterability of Sialons

Alan Arias

APRIL 1979

NASA

NASA Technical Paper 1382

Effect of Oxygen-Nitrogen Ratio on Sinterability of Sialons

Alan Arias
Lewis Research Center
Cleveland, Ohio

National Aeronautics
and Space Administration

Scientific and Technical
Information Office

1979

SUMMARY

The present investigation was undertaken to determine the effect of the oxygen to nitrogen ratio (O/N) on the sinterability of a series of Sialons defined by the equation $Si_{2.55}Al_{0.6}O_yN_{4-0.667y}$, where y ranges from 0.57 to 1.92. These Sialons were compounded by mixing milled powders of α-silicon nitride (α-Si_3N_4), aluminum nitride (AlN), and Silica (SiO_2). Bars cold pressed from these mixtures were pressureless sintered for 4 hours in stagnant nitrogen at temperatures from 1670° to 1830° C. For comparison, the Sialons of the same compositions were made by hot pressing at 1750° C and 27.6 megapascals (4000 psi) for 1 hour in nitrogen.

Density-as-a-function-of sintering temperature plots showed that all the Sialons reached their greatest densities on pressureless sintering at about 1760° C. The density-as-a-function-of temperature plots of some of the Sialons had density maxima at this temperature, reflecting the combined effects of sintering and decomposition, both of which increase with temperature.

From comparisons of pressureless-sintered and hot-pressed densities, it is concluded that optimum sinterability, as evidenced by pressureless-sintered densities of about 98 percent of theoretical, occurs at O/N from about 0.2 to 0.3.

During the pressureless sintering of groups of Sialon bars of different compositions, material transport occurs in the vapor phase, and the Sialons may gain or lose weight, depending on their compositions and the sintering temperature. The weight changes can be controlled by sintering the Sialons under the cover of mixtures of coarse Si_3N_4 and SiO_2 powders. With or without covers, however, the Sialons decomposed severely on pressureless sintering at ~1830° C, evolving silicon and smaller amounts of aluminum.

INTRODUCTION

It has been reported that to bring about pressureless sintering of β'-Sialons (refs. 1 and 2), additives such as magnesia or yttria are required (ref. 3). Unfortunately, additives may impair some of the desirable properties of these Sialons. For instance, in a recent investigation by this author (ref. 4) it was revealed that the oxidation resistance of Sialons decreases with increasing yttria additions. It is surmised, therefore, that Sialons without additives should have better oxidation resistance. Before the oxidation resistance and other properties can be determined, however, processes must be developed for the consolidation of these Sialons.

The objective of the present investigation was to determine the effect of varying the oxygen to nitrogen ratio (O/N) on the sinterability of Sialons compounded without additives. To carry out this objective, Sialons were compounded from separately ball-milled α-silicon nitride (α-Si_3N_4), aluminum nitride (AlN), and silica (SiO_2). In the Sialons investigated the silicon to aluminum ratio (Si/Al) was kept constant while the O/N ratio was varied. This means that the term Sialon as used herein refers to compositions of silicon, aluminum, oxygen, and nitrogen within the quarternary system Si_3N_4-AlN-Al_2O_4-SiO_2, as defined in reference 5. Part of the so-called "behavior diagram" for this quarternary system is reproduced in figure 1. As indicated in this figure, the Sialons used in the present investigation have compositions in the β'-Sialon and adjacent fields.

Sialon bars were sintered at various temperatures and sintering conditions. Density, shrinkage, and weight losses were measured to determine the effects of O/N and processing conditions on sinterability. Chemical, microscopic, microprobe, and X-ray diffraction analyses were performed to characterize the pressureless-sintered Sialons. For comparison, the Sialon compositions were also consolidated by hot pressing.

MATERIALS, EQUIPMENT, AND PROCEDURE

The materials used in this investigation were all -325 mesh powders of α-Si_3N_4, AlN, and SiO_2. These materials are characterized in table I.

The equipment used in this investigation has been described at length in reference 4. Briefly, it consisted of 1.5-liter, nickel-lined ball mills with nickel shot as grinding media; 1.4-liter alumina ball mills with alumina balls as grinding media; and standard laboratory equipment (presses, dies, furnaces, analytical equipment, etc.).

The procedures used for the preparation and testing of the Sialon specimens are outlined in the flow diagram of figure 2. These procedures will be outlined very briefly, except where they differ significantly from the procedures used in a previous investigation on Sialons (ref. 4).

Milling. - The α-Si_3N_4 and the SiO_2 were separately milled with water as the milling fluid in the nickel-lined mills for 300 and 130 hours, respectively. The AlN was milled with n-heptane as the milling fluid in the alumina mill for 100 hours.

During the ball milling of α-Si_3N_4 the mill pressure increased because of gas evolution. This required that the pressure be relieved several times during the run to prevent bursting of the mill. Because of this pressure buildup, a separate milling run was made to measure the pressure increase and to collect gas samples for analysis by mass spectrometry.

Removal of pickup. - During ball milling, materials resulting from the wear of balls and mills (pickup) contaminate the milled powders. In most cases this pickup is detrimental to the properties of the Sialon and must be removed. The pickups in the milled α-Si_3N_4 and SiO_2 were removed magnetically. Then the milled powders were leached with reagent grade nitric acid, washed with water, centrifuged, and vacuum dried at about 100° C. The milled AlN was dried in a stream of dry nitrogen without removing the Al_2O_3 pickup. In all cases after pulverizing the dry powder cakes in a Waring blendor, the powders were kept in air-tight containers until ready for use.

Chemical and BET analyses. - The as-received powders were analyzed for oxygen and carbon. Both the as-received and milled powders were analyzed spectrographically for trace elements. For milled powders the chemical analyses for oxygen and carbon are needed to calculate the amounts of each of the powders required to compound a given Sialon. However, as will be seen in the sections that follow, the Sialon powder mixtures are mixed with temporary binder and ethanol, followed by cold pressing and removal of the temporary binder by heating at 450° C. Therefore, before analysis each of the three milled powders was mixed with temporary binder and ethanol, dried, and heated as if it were a Sialon mixture. The so-treated powders were then analyzed for oxygen and carbon.

The specific surface areas of the powders were determined by the BET (Brunauer, Emmett, and Teller) method.

Mixing. - The calculated amounts of milled α-Si_3N_4, milled AlN, and milled SiO_2 were mixed with 5 weight percent, DC-705 silicone oil (as a temporary binder) and 70 weight percent of 200-proof ethanol in a polyethylene bottle with the aid of stainless-steel balls. After mixing for 1 hour, the resulting slurry was dried at about 100° C, and the resulting powder agglomerates were pulverized in a Waring blendor.

Cold pressuring. - The powder mixtures were shaped into bars approximately 3.81 by 0.92 by 0.47 centimeter by cold pressing at 207 megapascals (30 ksi). These bars were then isostatically cold pressed at 483 megapascals (70 ksi).

Removing the temporary binder. - The silicone oil binder was removed from the bars by heating them slowly (for about 2 hr) in flowing nitrogen to 450° C and holding them at that temperature for 1 hour.

Sintering. - In preparation for each sintering run, Sialon bars of all six compositions were dried, weighed in an analytical balance, measured with a micrometer, and placed together in a tungsten sintering boat with a close fitting (but not gas tight) cover. This boat was placed in a larger sintering boat fitted with a cover with an opening for a thermocouple. All sintering was done in a furnace with graphite heating elements for 4 hours in stagnant nitrogen at a 34.5-kilopascal (5-psi) gage pressure. Various sintering runs were made at temperatures from 1670° to 1830° C. The sintering temperatures were monitored with W/W-26Re thermocouples. In one series of sintering runs at 1760° C the Sialon bars were covered with various mixtures of as-received α-Si_3N_4 and SiO_2 (table I). All of the sintered bars were measured and weighed to calculate shrinkage and weight losses during sintering. The sintered specimens were ground into 0.635- by 0.318- by 2.54-centimeter bars.

Characterization of sintered bars. - The densities of most of the surface-ground Sialon bars were determined by water immersion. In some cases the bars were too porous to use this method and their densities were determined from their weights and dimensions. Chemical, X-ray, scanning electron microscopy (SEM), microprobe, and optical microscopy analyses of the sintered and ground Sialons were done.

Hot pressing. - To compare densities and compositions, the same series of Sialons were prepared by hot pressing. The powder mixtures for hot pressing were the same as those used for sintering except that after mixing with the temporary binder, drying, and pulverizing in a Waring blendor the resulting mixtures were heated (without cold pressing them) to remove the temporary binder. The mixtures were hot pressed three at a time in a double-acting graphite die (described in ref. 6, p. 6) at 1750° ± 25° C and 27.6 megapascals (4000 psi) for 1 hour in flowing nitrogen.

RESULTS AND DISCUSSION

Sialons Investigated

The six Sialon compositions used in this investigation were compounded from the finely milled α-Si_3N_4, AlN, and SiO_2 powders characterized in table II. These powders were compounded into Sialon compositions having the general formula.

$$Si_{2.55}Al_{0.6}O_yN_{4-0.667y}$$

where y varied from 0.57 to 1.92 and, correspondingly, the molar O/N varied from 0.157 to 0.706. It may be noted that in this equation the sum of the cationic charges[1] is 12 and, regardless of the value of y, the sum of the anionic charges[1] is also 12. Therefore, these compositions are Sialons (ref. 5) but only one, that for which $y = 0.6$, is a β'-Sialon.

The compositions of the Sialons investigated and their designations are listed in table III. The locations of these compositions in the Si_3N_4-AlN-Al_2O_3-SiO_2 "idealized behavior" diagram (ref. 5) are shown in figure 1. The coordinates locating these compositions are given by the bracketed fractions (e.g. [0.095/0.905]) in the fourth column of table III. The coordinates for any given composition can also be obtained by dividing

---

[1] Assuming values of Si^{+4}, Al^{+3}, O^{-2}, and N^{-3}.

the subscripts of Si, Al, O, and N in the Sialon formula by the corresponding subscripts in the diagram of figure 1, that is, by 3, 4, 6, and 4, respectively. As seen in the plot the compositions of the Sialons investigated range from just below the β' field to near the O' field with only Sialon B being a β'-Sialon. The common factor in all these compositions is that the Si/Al is constant. The O/N was varied for each composition to study the effect of this ratio on the sinterability of Sialons. The choice of O/N for study was predicted on the commonly accepted view that Sialon sintering involves a glass phase. The amount, composition, and properties of this glass phase and, therefore, the sinterability of the Sialon can be expected to depend on O/N. This sinterability was ascertained mainly from density measurements and to a lesser extent from the microstructure of the sintered Sialons. Although shrinkage would seem to be a good method of determining sinterability, it was found to be usually unreliable, for reasons to be explained later.

Effect of Sintering Temperature and Oxygen to Nitrogen Ratio on Sinterability

The plots in figure 3 show the effects of sintering temperature on the densities of the six Sialons investigated. In general, all attained their maximum densities at about 1760° C. Only the β'-Sialon (B) shows a small increase in density at higher sintering temperatures; the density of Sialon C remains constant; and those of the other Sialons decrease at temperatures above 1760° C. The dashed lines in the plots of Sialons A (lowest O/N) and F (highest O/N) indicate decomposition and a concomitant (and only roughly measurable) decrease in density at sintering temperatures above about 1800° C. Sometimes this decomposition could be detected visually (by a bloated or clinker-like appearance). However, Sialons D and E, whose plots also show a drop in density with increasing sintering temperatures, appeared normal. In these cases the decrease in density is caused by an increase in pore size, as the photomicrographs of Sialon E in figure 4 show. Thus, the maxima in the plots of figure 3 are the result of two competing and temperature-dependent processes: (1) increasing densification with increasing temperature due to sintering and (2) decreasing densification with increasing temperature due to gas evolution (to be discussed later) resulting from the decomposition of or reactions in the Sialons. Since Sialons sinter with the aid of a liquid phase, the maxima can be expected to be also composition dependent. However, other factors such as the strength of the Sialon at the sintering temperature can be expected to determine the temperature at which the maxima occur.

Figure 5 shows the effect of O/N on the densities of the six Sialons after sintering at 1760° C. For comparison, it also shows the densities of the same Sialons after hot pressing at 1750° C and a plot of the ratio of the sintered to hot-pressed densities. It follows from this figure that the pressureless-sintered Sialons achieve maximum densification at O/N between about 0.2 and about 0.3, that is, between Sialon compositions C and D. This conclusion cannot be so readily confirmed by observation of the corresponding Sialon microstructures shown in figure 6 because in the low O/N Sialons low density results from microporosity, whereas in the high O/N Sialons it results from very large pores. On the other hand, as shown in the microphotographs of figure 7, hot-pressed Sialons appear to be quite dense, particularly compositions B, C, and D. For practical purposes these three hot-pressed compositions may be considered to be fully densified. On this basis, the pressureless-sintered Sialons C and D were densified to 98 percent of their theoretical densities whereas the β'-Sialon (Sialon B) was densified to only 94.5 percent of its theoretical density. Therefore, optimum sintering is obtained with compositions just above the β' field.

Weight Losses and Shrinkage During Pressureless Sintering

All the bars were carefully weighed and measured before and after sintering to determine weight losses and shrinkage. However, the after-sintering measurements were rendered inaccurate by the presence of powdery material on the surface of the specimens and sometimes also by warpage. In spite of these inaccuracies, it may be stated that weight losses increase with increasing sintering temperature and O/N. For example, the weight loss of composition C varied from 1.6 percent after 1700° C sintering to 10.2 percent after 1830° C sintering, as contrasted to 12.6 and 56 percent, respectively, for composition F. By comparison, composition A gained 2.3 weight percent after sintering at 1700° C and lost 9.6 weight percent after the 1830° C sintering. Composition B displayed similar behavior, that is, it gained weight on sintering at low temperatures and lost weight on sintering at higher temperatures. This weight gain phenomena when sintering bars of different compositions together means that there is material transport in the vapor phase during sintering even at the lowest sintering temperatures (1670° C) used in this investigation. It has been surmised (ref. 4) that on synthesizing Sialons at high temperatures the vapor phase may contain SiO, CO, and nitrogen. However, it appears from the present investigation that free silicon is also formed. In fact, in the 1830° C sintering run some of the specimens (particularly Sialons A and B) were covered with small metallic beads. As much as 0.5 gram of beads were scraped off some of them. Chemical analysis showed the beads to be silicon with about 1 weight percent aluminum, 1.5 weight percent oxygen, and 0.08 weight percent carbon. The original Si/Al of all Sialons is 4.424, on a weight basis, as contrasted with a ratio of about 96 in the beads. Silicon beads produced as a result of sintering

Sialons at 1800° C were also reported in reference 7. The formation of silicon beads on sintering higher-aluminum-content Sialons at 1750° to 1800° C was noted in reference 7, but no aluminum was reported in that work. Apparently, this silicon loss also occurs at the lower sintering temperatures because the outer tungsten sintering boat gained weight in all the sintering runs. The presence of silicon in the tungsten was confirmed by X-ray analysis. The Sialon weight losses can probably be eliminated by sintering under high nitrogen pressure, but this was not attempted in the present investigation. However, weight losses and some of the problems associated with them can be controlled by procedures described later on in this paper.

The weight losses mentioned above render the sintering shrinkage measurements inaccurate. This is because the overall specimen shrinkage is that caused by sintering plus that resulting from the loss of material. In general, though, the densest Sialons shrink the most, as expected. The linear shrinkages on sintering at 1760° C, for example, vary from 13 percent for Sialon B to 15 percent for Sialon D.

Sintering of Sialons in Mixtures of Si_3N_4 and SiO_2 Powders

The weight loss on sintering Sialons could be a problem if the Sialons were to be fabricated into thin sections such as those found in ceramic heat exchangers. For this reason experiments were designed to control this weight loss. These experiments consisted of sintering the Sialons in various mixtures of the as-received α-Si_3N_4 and SiO_2 characterized in table I. The various powder mixtures or sintering covers used are listed in table IV. This table also shows the results obtained after sintering the Sialons in these various mixtures. All of the Sialons were sintered at 1760° C for 4 hours in stagnant nitrogen. For comparison, a sintering run without the protective Si_3N_4-SiO_2 powder cover is also included in table IV.

The data in table IV show that, in general, the densities of the specimens are about the same for any given Sialon, regardless of the sintering cover (or lack of it). However, weight losses were considerably reduced by the use of sintering covers. In fact, the data in table IV show that cover mixtures can be chosen that will cause anywhere from a slight weight loss to a slight weight gain in all the Sialons except F. Even in Sialon F the weight loss can be made quite small. In addition, because of the controlled weight losses, there is no powdery material on the specimens after sintering, and shrinkage measurements are more reliable. For this reason, shrinkage and weight losses are included in table IV. Only for Sialon C are oxygen and carbon analyses included. The carbon content remains in the ppm range, but the oxygen increases slightly with increasing SiO_2 in the cover, and the oxygen increase is practically nil at near zero weight loss. Presumably, the other Sialons behave similarly. However, it would be a relatively simple matter to compound the Sialon so as to compensate for oxygen pickup on sintering.

An added advantage of the Si_3N_4-SiO_2 sintering covers used in this investigation is that they are friable and do not stick to the Sialon specimens. These sintering covers can probably be reused but were not in this investigation.

In addition to the experiments already described, an attempt was made to sinter the Sialons at 1830° C under cover of a 90 Si_3N_4 + 10 SiO_2 mixture. After sintering at this temperature the sintering cover had a weight loss of about 50 percent as compared with a 6.4-percent weight loss after sintering at 1760° C. Sialons A, B, and C had weight losses of about 2 percent and the same density (3.03 g/cm^3); Sialon D was slightly bloated; and Sialons E and F were badly bloated and spongy. Also, there were metal beads on and between specimens (as had occurred in the 1830° C run without a cover) as well as throughout the sintering cover. The total weight of beads recovered in this run was about 5 grams or about 4.6 weight percent of the total weight of Sialons and sintering cover. Chemical analysis of these beads showed that they were similar to the ones previously described.

Microstructures

Figure 6 shows photomicrographs of the six Sialons that were pressureless sintered at 1760° C without a powder cover. These photomicrographs all show dark looking holes or pull outs, a rounded, light gray phase, which is about the same size and shape as the holes, and small amounts of a metallic looking phase. The sizes of the holes and light gray phase increase with increasing O/N, but the amount of the metallic phase is about the same in all the Sialons. The matrices of the low O/N Sialons (A to C) are featureless. This was expected because X-ray diffraction showed them to be practically all β' phase (table III). X-ray diffraction also showed that Sialons D to F each had two phases. This agrees with the number of phases seen in the matrices of their photomicrographs. However, Sialon D should show three phases (β', O', and X), according to the diagram of figure 1. The reason for this discrepancy is unknown, but it should be noted that figure 1 is an idealized behavior diagram and not a real equilibrium phase diagram; therefore, the results obtained may be expected to depend on experimental conditions.

The rounded, light gray phase is quite abundant in Sialon F. However, it was not detected by X-ray diffraction, and microprobe analysis indicated that it contained higher aluminum and oxygen and lower silicon than the matrix. From the evidence gathered so far, it appears that the light gray areas may be either a glass or debris jammed into holes during polishing. The bright metallic looking areas are, according to microprobe analysis, a silicon-base alloy or intermetallic compound.

The photomicrographs of the hot-pressed Sialons in figure 7 show very little porosity and very small amounts of the bright phase. Only the high O/N Sialons (D to F) appear to have the rounded, light gray phase, but in a much finer size and in much smaller amounts than in the pressureless-sintered Sialons.

Scanning electron microscopy analyses of the fracture surfaces of both the pressureless-sintered and the hot-pressed Sialons showed them to have equiaxed grains about 1.1 micrometers average diameter.

Chemical and Surface-Area Analyses of Powders and Implications

Table I shows the chemical analyses of the as-received α-Si_3M_4, AlN, and SiO_2 powders, and table II those of the same powders after milling. Table II also includes some milling and processing data. Comparison of the data in tables I and II shows that after milling and leaching the metallic impurities in the α-Si_3N_4 were reduced. The metallic impurities of the AlN, particularly cobalt and chromium, increased slightly during milling because of pickup from balls and mill. From the weight loss of balls and mill, it was calculated that the AlN picked up about 1 weight percent Al_2O_3. The main effect of milling and leaching on the metallic composition of the SiO_2 was the pickup of 900 ppm of nickel.

Comparison of the data in tables I and II also shows that, after milling, leaching, drying, mixing with the temporary binder, and burning off the binder, oxygen and carbon contents of all three powders increased. From the chemical analyses of the milled powders, only the silicon, aluminum, oxygen, and carbon were taken into account for computing the amounts of powders required for compounding the Sialons. In these computations it was assumed that all the carbon would react with silica to form silicon and carbon monoxides (ref. 4). Spectrographically determined metallic impurities other than silicon and aluminum were regarded as part of the major metallic elements (Si and Al) in the powders.

During ball milling, the specific surface areas of the α-Si_3N_4, AlN, and SiO_2 powders were increased 3.4, 4.5, and 29.5 times, respectively. The specific surface area of the α-Si_3N_4 (20.33 m^2/g) produced in this investigation is twice that of a milled β-Si_3N_4 produced under the same conditions in another investigation (ref. 4). It is surmised that the larger specific surface area of the α-Si_3N_4 may result from its chemical reaction with the water used as milling fluid. This reaction was evidenced by the increase in mill pressure caused by gas evolution during milling. During a 300-hour milling run the mill pressure increased by 1054 kilopascals (152.8 psi). Further prolonged milling caused only a small pressure increase. In contrast, no pressure increase was noted on milling the β-Si_3N_4. Mass spectrometer analysis of the gases evolved during ball milling of α-Si_3N_4 showed it to be 99.9 volume percent hydrogen with traces of methane (CH_4) and ethane (C_2H_6). It is surmised that the hydrogen is formed by reaction of water with free silicon in the as-received α-Si_3N_4. From the mill pressure increase and the known head space of the ball mill (476 cm^3), it is calculated that the as-received α-Si_3N_4 contained about 1.4 weight percent free silicon. Most of the free silicon is converted to SiO_2 on milling; therefore, the silicon-base alloy or intermetallic compound seen in the Sialon photomicrographs is not free silicon from the raw Si_3N_4, but probably comes from decomposed Si_3N_4. It is surmised that Sialons made from as-received α-Si_3N_4 would have more of the metallic phase. However, this could not be checked out because the same Sialons compounded from the as-received powders yielded unsintered, crumbly specimens. From these results it is concluded that, in order to pressureless sinter Sialons with optimum densities without sintering aids, very find powders are required.

Chemical Analysis of Sintered Sialons and Implications

Chemical analyses of both the pressureless-sintered and hot-pressed Sialons are shown in table III. For comparison the calculated O/N of the Sialons are also included in this table.

Except for composition A, the oxygen analysis of the pressureless-sintered Sialons is within 7 percent of the values calculated from the Sialon formulas. Considering the cumulative analytical errors involved, the agreement is good. Again, except for composition A, the pressureless-sintered Sialons show very little residual carbon. Thus, the assumption that carbon reacts with SiO_2 to form the monoxides of carbon and silicon (ref. 4) appears to be correct, except that in the case of composition A only part of the carbon appears to have reacted. The reason composition A retained much of its carbon is unclear, but it may be due to the very small amounts of SiO_2 in this Sialon. In fact, if the residual 0.32 weight percent carbon were assumed to react with SiO_2 as predicted, the oxygen content of Sialon A would be reduced to about 6 weight percent. This is within 3 percent of the calculated value.

The main point to consider, however, is that the oxygen analysis of Sialon A is just about the same as that of Sialon B, even though the latter was sintered to a much higher density (see fig. 3). Microprobe analyses of Sialons A, B, and C gave Si/Al's of 3.78, 4.44, and 4.57, respectively, as compared with a calculated value of 4.424 (on a weight basis) for all the Sialons investigated. Therefore, it appears that Sialon A did not sinter despite its relatively high O/N because, as a result of the Si/Al shift to higher aluminum content, the resulting composition was still below the β' field.

The oxygen analyses of the hot-pressed bars are invariably higher than those of the corresponding, pressureless-sintered bars. The residual carbon analyses of the surface ground bars are also higher than expected. It is doubtful that the residual carbon comes from the carbon dies because the reaction would be confined to the surface of the bars and these surfaces are ground off before analyses. Rather, it is surmised that, because pressure is applied during sintering, the escape of SiO and CO (as well as that of Si and N_2) is hindered. On the other hand, because of the high concentration of carbon there, relatively large amounts of SiO and CO would tend to form on the surface of the bars. The net result of these two additive effects (hindered SiO and CO evolution from the interior and their relatively high concentration on the surface of the bars) hindered the reaction $SiO_2 + C \rightleftarrows SiO + CO$ inside the bars. Since more SiO_2 would be retained in the hot-pressed than in the presureless-sintered Sialons, the hot-pressed Sailons would behave as if their O/N were increased. This would explain why compositions A and B hot pressed to relatively high densities. Shifting the O/N to higher values has a greater effect on densification in the lower O/N range near the β' field, as figure 5 indicates.

SUMMARY OF RESULTS AND CONCLUSIONS

The main objective of the present investigation was to determine the effect of the oxygen to nitrogen ratio (O/N) on the sinterability of Sialons of the formula. $Si_{2.55}Al_{0.6}O_yN_{4-0.667y}$ where y varied from 0.57 to 1.92. The results and conclusions drawn therefrom can be summarized as follows:

1. Density measurements on Sialons of varying O/N, pressureless sintered in stagnant nitrogen for 4 hours at temperatures from 1670° to 1830° C, showed that maximum densities for all six Sialons investigated occurred at about 1760° C.

Comparisons of the densities of the 1760° C, pressureless-sintered Sialons with those of the 1750° C, hot-pressed Sialons showed that optimum sinterability, as evidenced by pressureless-sintered Sialon densities of about 98 percent of theoretical, occurs in the O/N range from about 0.2 to about 0.3. The lowest O/N in this range is just above the β'-Sialon field. Sialons below this field do not sinter well.

2. On presureless sintering together Sialons of different compositions at low temperatures, some of the low O/N Sialons gained weight, and the high O/N Sialons lost weight. At high sintering temperatures all Sialons lost weight. It is concluded that gas-phase material transport occurs during presureless sintering of Sialons.

3. On pressureless sintering the Sialons under cover of mixtures of -325-mesh, α-Si_3N_4 with 0 to 20 weight percent of -325-mesh SiO_2, the weight losses of all the Sialons decreased (or their weight gains increased) with increasing SiO_2 in the sintering

cover. It is concluded that the weight changes that occur during pressureless sintering can be controlled in most Sialons by sintering them under cover of powdered mixtures of coarse Si_3N_4 and SiO_2.

4. On pressureless sintering at about 1830° C the Sialons become coated with beads of a high-silicon, low-aluminum alloy. It is surmised that
   a. The observed silicon results from the decomposition of Si_3N_4 (or the Sialon)
   b. In Sialons with O/N smaller than in β'-Sialons, the loss of silicon may cause a Sialon composition shift towards higher aluminum content and, therefore, decreased sinterability
   c. The silicon resulting from decomposition of Si_3N_4 (or the Sialon) is, at least in part, the metallic phase observed in Sialon photomicrographs.

5. Chemical analyses of hot-pressed Sialons show oxygen and carbon in higher than expected values on the basis of assumed reactions between carbon and silica. It is surmised that the application of pressure during sintering reduces decomposition and the formation of reaction gases so that the O/N and, therefore, the sinterability increase.

6. On ball milling α-Si_3N_4 in water, hydrogen is evolved. It is surmised that this hydrogen is produced by the reaction of water with free silicon in the α-Si_3N_4 used.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 5, 1978,
505-01.

REFERENCES

1. Jack, K. H.; and Wilson, W. I.: Ceramics Based on the Si-Al-O-N and Related Systems. Nature (London), Phys. Sci., vol. 238, no. 80, 1972, pp. 28-29.

2. Oyama, Y.; and Kamigaito, O.: Sintered Bodies of the Silicon Nitride-Alumina System. Yogyo Kyokai Shi (Japan), vol. 80, no. 8, 1972, pp. 327-336.

3. Layden, G. K.: Development of Sialon Materials (R77-912184-21, United Technologies Research Center; NASA Contract NAS3-19712.) NASA CR-135290, 1977.

4. Arias, A.: Pressureless Sintered Sialons with Low Amounts of Sintering Aid. NASA TP-1246, 1978.

5. Jack, K. H.: Sialons and Related Nitrogen Ceramics. J. Mater. Sci., vol. II, 1976, pp. 1135-1158.

6. Arias, A.: Investigation of Thermal Shock Resistance of Zirconia with Metal Additions. NASA TN D-2464, 1964.

7. Layden, G. K.: Pressureless Sintering of SiAlON Gas Turbine Components. NADC-75207-30, Naval Air Development Center, 1977.

TABLE I. - CHARACTERIZATION OF RAW MATERIALS

Material	Source	Manufacturer's designation	Size	Specific surface area, m^2/g	Chemical analysis		Spectrographic analysis or manufacturer's specification, ppm (unless otherwise noted)
					Oxygen content, wt%	Carbon content, wt%	
α-Si_3N_4	Kawecki Berylco Industries, Inc.	CP 85	-325 mesh	5.223	1.75	0.26	Si major, 0.3 wt% Al, 0.3 wt% Ca, 200 Cr, 140 Cu, 0.3 wt% Fe, 140 Mg, 260 Mn, 300 Mo, 360 Ni, 530 Ti, 120 V, 180 Zr.
AlN	Atlantic Equipment Engineers	AL 106	-325 mesh	1.83	2.39	0.11	Al major, 70 Ca, 550 Co, 350 Cr, 90 Cu, 350 Fe, 130 Mg, 80 Mn, 250 Mo, 160 Ni, 240 Si, 190 Ti, 640 W, 140 Zr.
SiO_2	Cerac Pure	S-1061	-325 mesh	0.92	(a)	0.012	Si major, 1000 Al, <10 Ca, 50 Cr, 120 Cu, 50 Fe, 190 Mg, 130 Mn, 90 Ti.

[a] Not determined.

TABLE II. - MILLING DATA AND CHARACTERIZATION OF MILLED POWDERS

Milling data					Characterization of milled powders				
Powder	Mill	Media	Fluid	Time, hr	Post-milling treatment	Specific surface, m^2/g	Chemical analysis		
							Oxygen content, wt% (a)	Carbon content, wt% (a)	Other elements, ppm (unless otherwise noted) (b)
α-Si_3N_4 (CP 85)	Nickel	Nickel shot	Distilled water	300	Leach, wash, dry	20.33	6.75	0.47	Si major, 0.3 wt% Al, 400 Ca, 110 Cr, 50 Cu, 0.1 wt% Fe, 60 Mg, 60 Mn, 100 Mo, 190 Ni, 170 Ti, 30 V, 30 W.
AlN (AL 106)	Alumina	Alumina	n-heptane	100	Dry	9.86	5.04	0.235	Al major, 160 Ca, 0.2 wt% Co, 0.1 wt% Cr, 80 Cu, 340 Fe, 720 Mg, 100 Mn, 380 Mo, 180 Ni, 870 Si, 50 Ti, 210 V, 690 W.
SiO_2 (S-1061)	Nickel	Nickel shot	Distilled water	130	Leach, wash, dry	27.1	(c)	0.600	Si major, 630 Al, 130 Ca, 70 Cr, 110 Cu, 80 Fe, 210 Mg, 900 Ni.

[a] Analyses were performed on powders treated with 5 wt% silicone oil in ethanol, mixed, then heated in flowing nitrogen for 1 hr.

[b] Values obtained by spectrographic analysis of the milled and dry powders.

[c] Not determined.

TABLE III. - SIALON COMPOSITIONS INVESTIGATED - PHASES PRESENT AND CHEMICAL ANALYSIS AFTER PRESSURELESS SINTERING AND AFTER HOT PRESSING

Sialon designation	Sialon formula aim	Calculated oxygen-to-nitrogen ratio		Calculated oxygen content, wt%	X-ray phases (a, b)	Chemical analysis				
						After pressureless sintering at 1760° C for 4 hr			After hot pressing at 1750° C	
		O/N, mole/mole	$\frac{O}{N}\times\frac{2}{3}$			Oxygen content, wt%	Carbon content, wt%	Other,[c] in ppm	Oxygen content, wt%	Carbon content, wt%
A	$Si_{2.55}Al_{0.6}O_{0.57}N_{3.62}$	0.1575	$\frac{0.095}{0.905}$	6.18	β'	6.75	0.32	(d)	6.68	0.19
B	$Si_{2.55}Al_{0.6}O_{0.6}N_{3.6}$	0.1667	$\frac{0.100}{0.900}$	6.49	β'	6.70	0.020	Al major, 370 Ca, 50 Co, 100 Cr, 60 Cu, 480 Fe, 140 Mg, 100 Mn, 80 Mo, 100 Ni, Si major, 130 Ti, 80 V, 110 Zr.	7.77	0.38
C	$Si_{2.55}Al_{0.6}O_{0.72}N_{3.52}$	0.2045	$\frac{0.120}{0.880}$	7.75	β' plus possible vvw X	8.26	0.014	Al major, 280 Ca, 80 Co, 100 Cr, 50 Cu, 340 Fe, 130 Mg, 130 Mn, 60 Mo, 60 Ni, Si major, 90 Ti, 50 V, 70 Zr.	8.69	0.22
D	$Si_{2.55}Al_{0.6}O_{1.0}N_{3.33}$	0.3000	$\frac{0.167}{0.833}$	10.63	β' plus vvw Si_2N_2O	10.70	0.018	(d)	11.6	0.36
E	$Si_{2.55}Al_{0.6}O_{1.44}N_{3.04}$	0.4737	$\frac{0.240}{0.760}$	15.02	β' plus m Si_2N_2O	15.02	0.020	(d)	15.5	0.36
F	$Si_{2.55}Al_{0.6}O_{1.92}N_{2.72}$	0.7059	$\frac{0.320}{0.680}$	19.61	β' plus s Si_2N_2O	19.9	0.016	(d)	20.4	0.24

[a] In pressureless sintered samples.

[b] vvw - very, very weak; m - medium; s - strong.

[c] Spectrographic analysis.

[d] Not determined.

TABLE IV. - EFFECT OF SINTERING COVER COMPOSITION ON THE PROPERTIES OF SIALONS

[Sintering conditions: 1760° C, for 4 hr in stagnant nitrogen.]

Sialon	Cover composition, Si_3N_4/SiO_2 (a)	Density, g, cm^{-3}	Shrinkage, percent	Weight loss, percent (b)	Oxygen content, wt%	Carbon content, wt%
A	0/0	2.80	9.1	3.18	----	-----
	100/0	2.82	10.5	.19	----	-----
	95/5	2.88	10.7	-1.0	----	-----
	90/10	2.93	11.3	-1.4	----	-----
	80/20	2.92	10.5	-1.5	----	-----
B	0/0	2.98	13.2	2.16	----	-----
	100/0	3.00	12.8	.87	----	-----
	95/5	3.01	12.7	-1.1	----	-----
	90/10	3.01	12.0	-1.2	----	-----
	80/20	3.02	12.0	-1.3	----	-----
C	0/0	3.08	13.6	3.20	8.26	0.020
	100/0	3.09	13.6	1.45	8.32	-----
	95/5	3.09	13.2	-.18	8.30	-----
	90/10	3.08	13.3	-.67	8.51	.032
	80/20	3.09	12.8	-1.02	8.60	-----
D	0/0	3.02	15.3	5.88	----	-----
	100/0	3.00	13.0	2.89	----	-----
	95/5	2.95	12.8	-.49	----	-----
	90/10	2.96	12.9	-.73	----	-----
	80/20	2.98	12.7	-1.2	----	-----
E	0/0	2.89	15.1	12.9	----	-----
	100/0	2.79	12.0	4.8	----	-----
	95/5	2.72	11.2	-.92	----	-----
	90/10	2.74	12.0	-.77	----	-----
	80/20	2.75	11.7	-1.57	----	-----
F	0/0	2.74	15.9	22.8	----	-----
	100/0	2.63	12.6	3.06	----	-----
	95/5	2.56	11.6	.76	----	-----
	90/10	2.61	12.4	.83	----	-----
	80/20	2.59	11.7	1.37	----	-----

[a] On a weight basis.

[b] Negative values indicate weight gains.

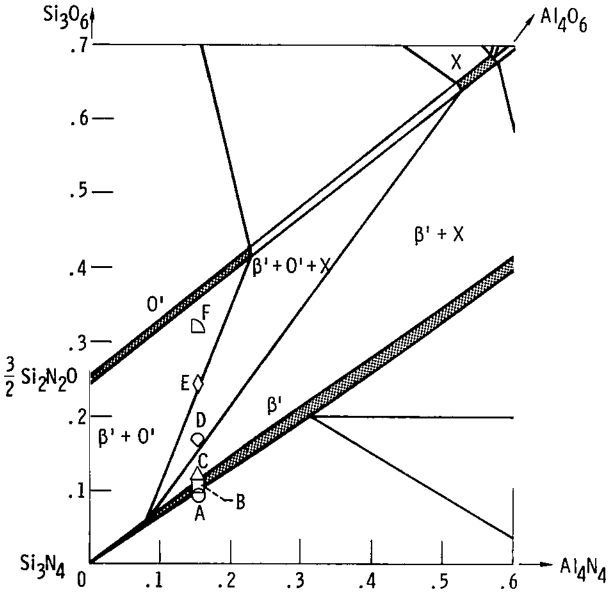


Figure 1. - Si_3N_4 corner of Si_3N_4-AlN-Al_2O_3-SiO_2 system (ref. 5) showing compositions investigated.

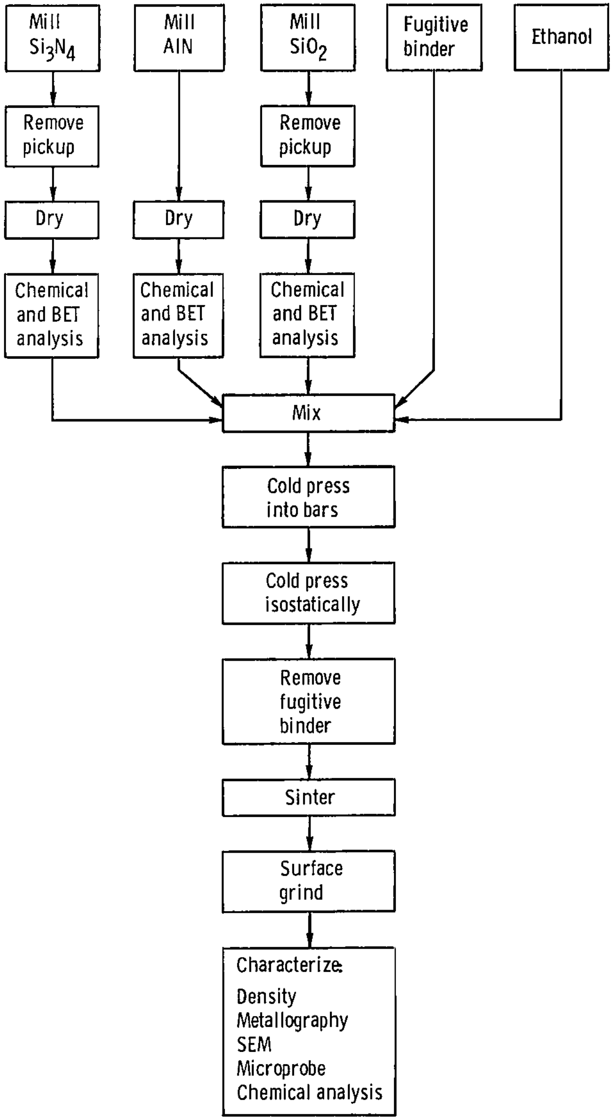


Figure 2. - Flow chart for the preparation and characterization of Sialons.

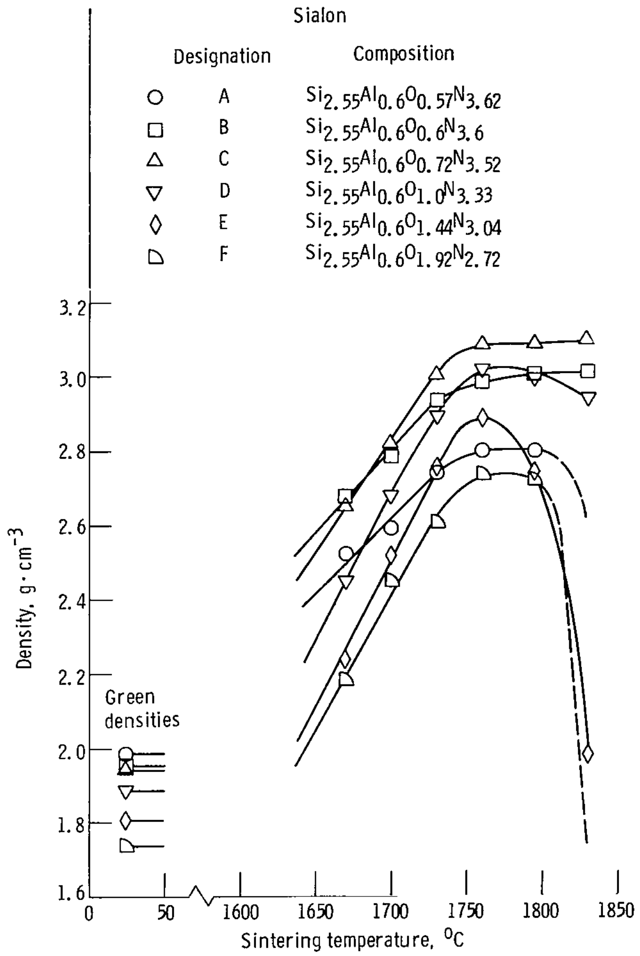
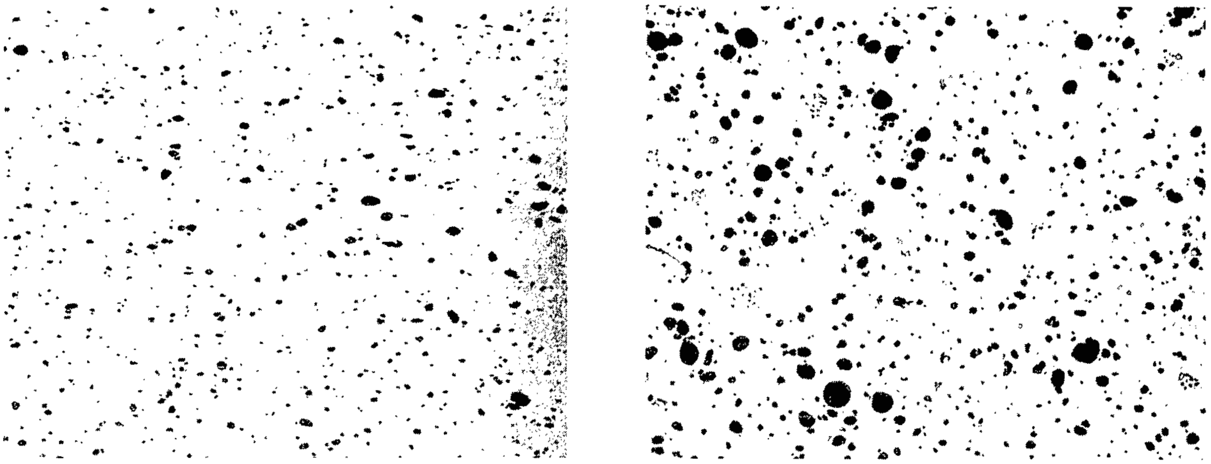


Figure 3. - Effect of sintering temperature on density of Sialons. Sintering time, 4 hours.



1760° C

1795° C

Figure 4. - Photomicrographs of Sialon E (table III) after pressureless sintering for 4 hours in stagnant nitrogen at the temperatures indicated. Magnification, X50; unetched.

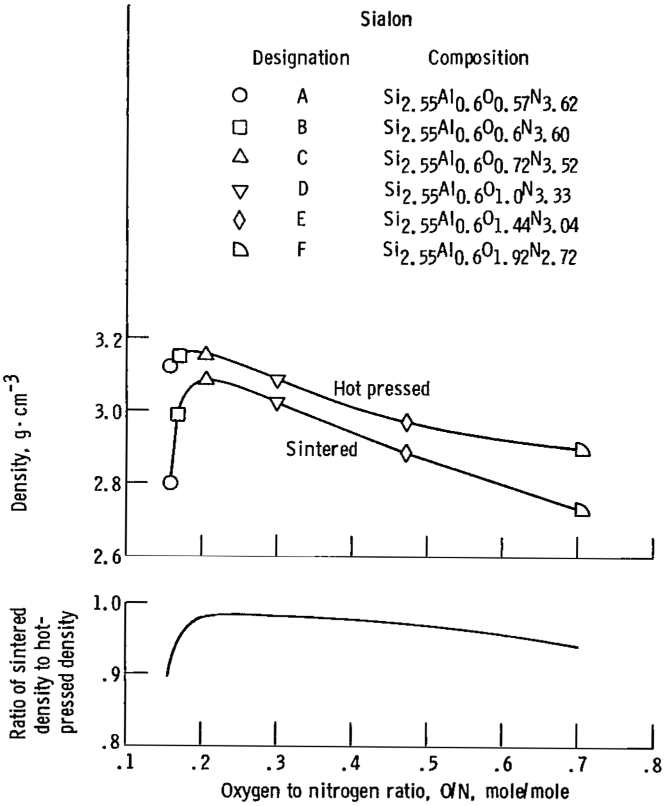
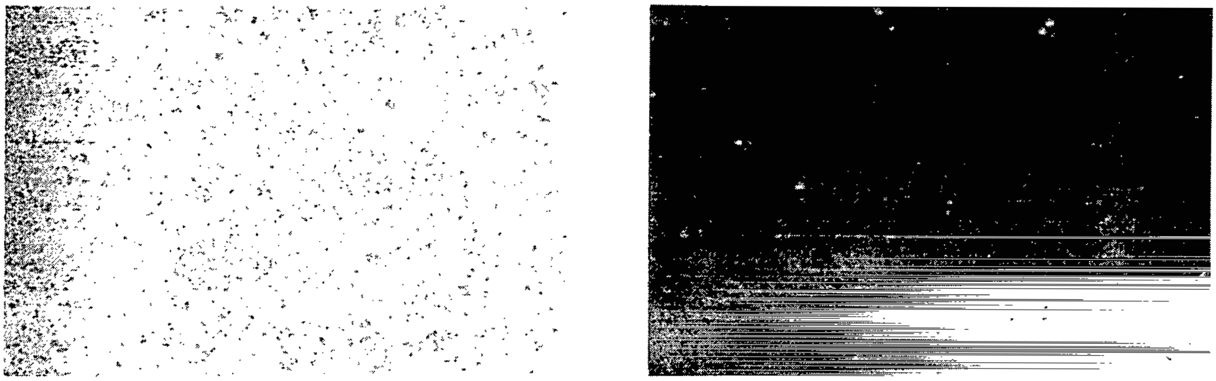
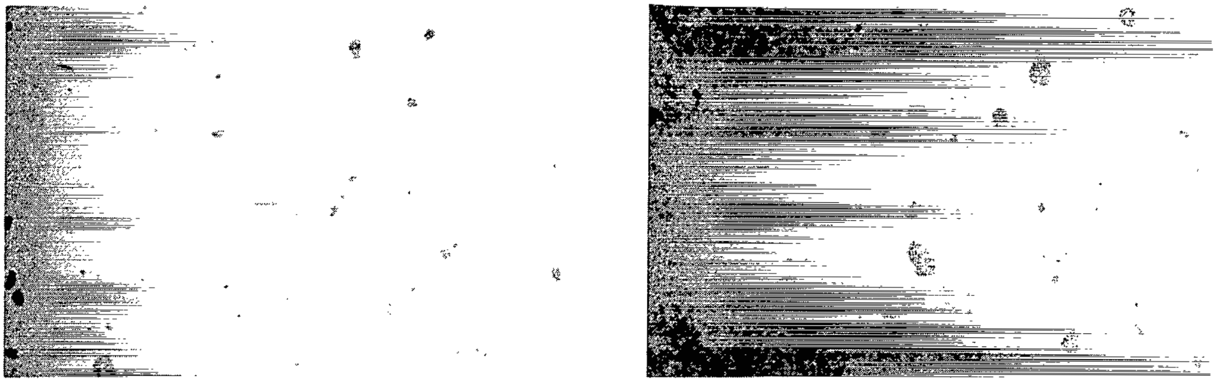


Figure 5. - Densities of Sialons after sintering at 1760° C and of those hot pressed at 1750° C as functions of oxygen to nitrogen ratio.



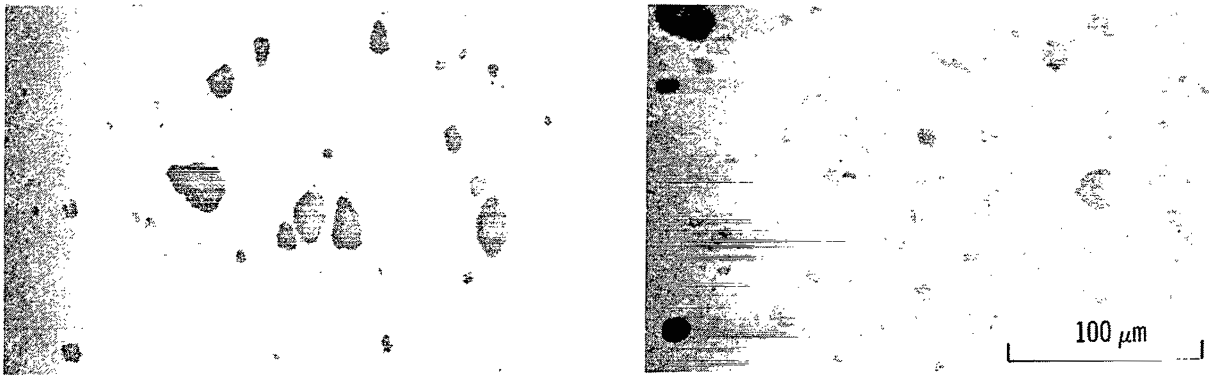
Sialon A; density, 2.80 g·cm^{-3}

Sialon B; density, 2.98 g·cm^{-3}



Sialon C; density, 3.08 g·cm^{-3}

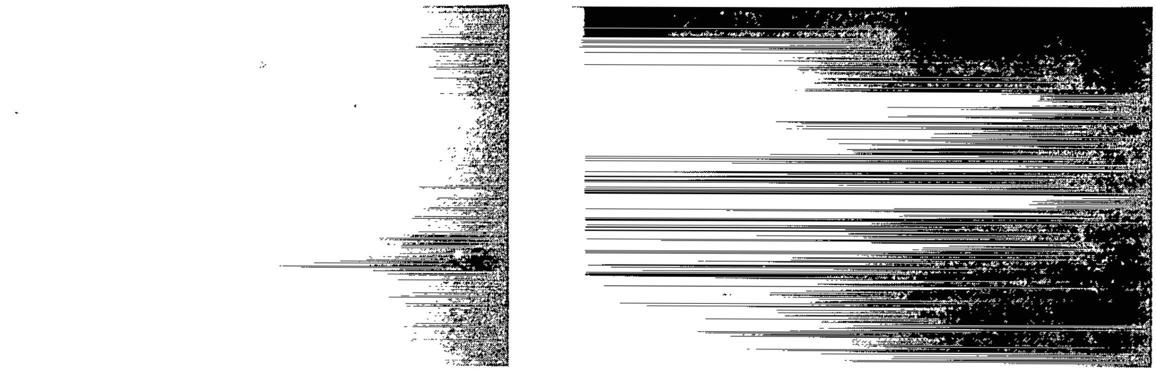
Sialon D; density, 3.02 g·cm^{-3}



Sialon E; density, 2.89 g·cm^{-3}

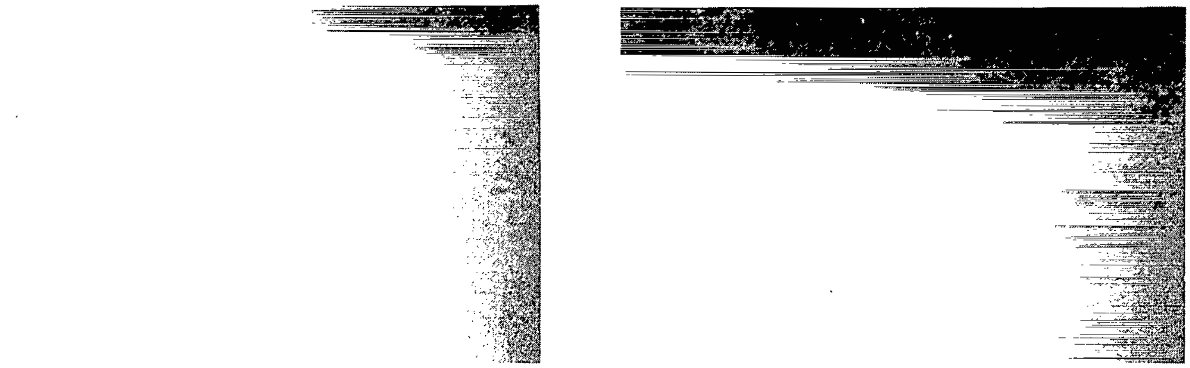
Sialon F; density, 2.74 g·cm^{-3}

Figure 6. - Photomicrographs of Sialons after pressureless sintering at 1760° C for 4 hours in stagnant nitrogen.



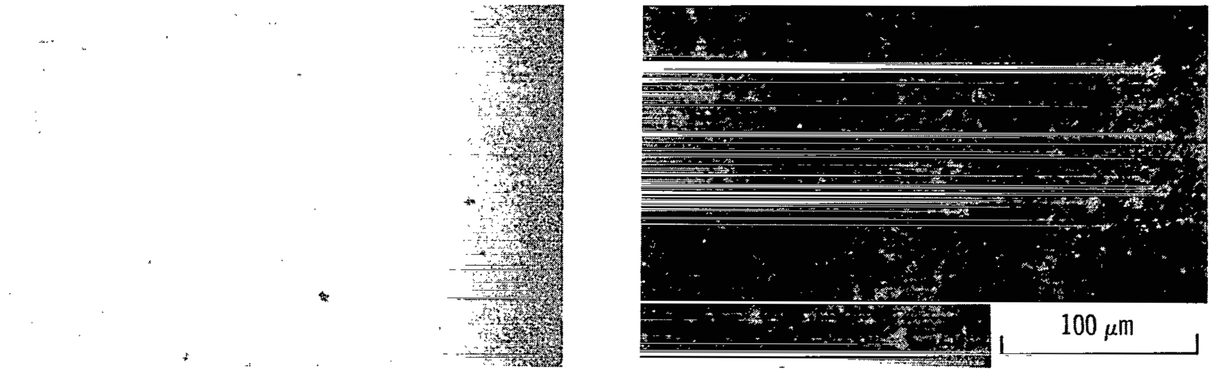
Sialon A; density, 3.12 g·cm^{-3}

Sialon B; density, 3.16 g·cm^{-3}



Sialon C; density, 3.16 g·cm^{-3}

Sialon D; density, 3.08 g·cm^{-3}



Sialon E; density, 2.97 g·cm^{-3}

Sialon F; density, 2.90 g·cm^{-3}

Figure 7. - Photomicrographs of Sialons after hot pressing at 1750° C and 27.6 megapascals (4000 psi) for 1 hour in flowing nitrogen.

1. Report No.
NASA TP-1382

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
EFFECT OF OXYGEN-NITROGEN RATIO ON SINTERABILITY OF SIALONS

5. Report Date
April 1979

6. Performing Organization Code

7. Author(s)
Alan Arias

8. Performing Organization Report No.
E-9814

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

10. Work Unit No.
505-01

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Technical Paper

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The effect of varying the sintering temperature and the oxygen to nitrogen ratio (O/N) on the sinterability of Sialons of the formula $Si_{2.55}Al_{0.6}O_yN_{4-0.667y}$ was investigated for y between 0.57 and 1.92 (O/N between 0.157 and 0.706). The Sialons reached maximum density on pressureless sintering for 4 hours at about 1760° C in nitrogen. Optimum sinterability with densities up to about 98 percent of theoretical was attained with negligible X-phase in the O/N range from about 0.2 to 0.3. On sintering at ~1830° C the Sialons decomposed with evolution of silicon and aluminum.

17. Key Words (Suggested by Author(s))
Ceramics
Sialons
Sintering

18. Distribution Statement
Unclassified - unlimited
STAR Category 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	23	A02

* For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1979

National Aeronautics and
Space Administration

Washington, D.C.
20546

5 1 1U,C, 022379 S00903DS
DEPT OF THE AIR FORCE
AF WEAPONS LABORATORY
ATTN: TECHNICAL LIBRARY (SUL)
KIRTLAND AFB NM 87117

NASA