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Dissolution of sintered silicon nitride bulk specimens for elemental analysis

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Heating bulk, sintered silicon nitride samples in an aqueous hydrofluoric–hydrochloric acid mixture is shown to decompose the silicon nitride. Subsequent addition of sulphuric acid and volatilization of fluorides permits total dissolution of the bulk specimens for analysis. The elemental compositions that were determined by inductively coupled plasma atomic emission and atomic absorption spectrometries agreed with the nominal sample composition and confirmed analyses performed by scanning transmission electron microscopy. Neutron activation determinations on the same samples are not believed to be as accurate as the spectrometric determinations. Furthermore, the precision of the neutron activation measurements were less satisfactory, especially for key elements such as yttrium.

1. Introduction

Silicon nitride ceramics have excellent strength retention at elevated temperatures and thus are being considered for a wide range of applications. To produce a formed shape the powder must be sintered, but sintering is very difficult because of the covalent nature of the bonding. In addition, silicon nitride tends to dissociate above 1700 °C. While dissociation can be reduced by utilizing a nitrogen overpressure, a small amount of various oxides are typically added to assist the sintering of the silicon nitride powder. Common additives include magnesia, yttria, alumina, ceria and their various combinations. At elevated temperatures between 1600 and 2000 °C these sintering aids react with each other and the surface oxides of the α-Si_3N_4 powder to form a liquid phase; α-Si_3N_4 dissolves in the liquid, and elongated β-Si_3N_4 grains then precipitate from solution. Upon cooling, the sintering aids concentrate in the grain boundaries and grain-boundary pockets. Another approach for fabricating a silicon nitride to full density is to nitride the silicon and then sinter. This is often referred to as reaction-bonded sintered silicon nitride. Typically iron is used as a nitriding catalyst; during high-temperature processing the iron is often converted into a silicide. Sintering aids, as discussed above, are used to attain full density.

Sintering aids are selected based upon the combination of ease of processing and desired high-temperature properties. For example, magnesia reduces the sintering temperature, but the creep properties are poor. Silicon nitride with yttria has very good creep properties, but sintering is more difficult because of the high viscosity of the liquid phase. A compromise is to utilize yttria and alumina as sintering aids. Because processing requires a number of steps (such as blending of powders, slip casting or injection moulding and sintering), determining the additive content, and impurities introduced during these operations becomes critical. Classical elemental analyses to determine the as-sintered elemental composition of these materials requires total dissolution of the sample. However, because silicon nitride is relatively inert and the sintered material is really a composite of silicon nitride and grain-boundary phase, dissolution techniques are complicated. Davis and Merkel [1] reported a technique for dissolving solid silicon nitride. The method is complex and repeatability data, to demonstrate precision and accuracy, are not reported. We wish to describe a simpler method for dissolution of sintered silicon nitride. The method has been applied to samples having known sintering aid levels. For this study we have also utilized scanning transmission electron microscopy (STEM) and neutron activation analysis to investigate the sintered silicon nitride samples. The results of these methods are compared with determinations performed by total dissolution followed by inductively coupled plasma atomic emission spectroscopy (ICP–AES), and atomic absorption spectroscopy (AAS).

2. Experimental procedure

2.1. Reagents

The reagents used were of analytical reagent grade, except as specified below. Baker Ultrex-grade hydrochloric acid was used to prepare solutions for determination of components at the parts per million (p.p.m.) level. Aqueous solutions were prepared using de-ionized water with a resistance of $> 18\ M\Omega$ cm (Class I water), which was obtained by post-treatment of the laboratory de-ionized water with a Barnstead

Nanopure II unit. ICP–AES and atomic absorption reference standards were prepared from Spex aqueous standards for plasma emission spectrometery.

2.2. Special equipment

Heavy-walled Teflon beakers were purchased from various scientific supply houses. Polypropylene volumetric ware was used for trace analysis. For trace work, plastic ware was cleaned by sequential overnight soaking in dilute HCl, then dilute HNO_3 followed by thorough washing with water. Teflon-lined nickel pressure vessels were used for the decomposition of the silicon nitride as described below.

2.3. ICP emission spectrometry

A Perkin–Elmer Plasma II inductively coupled plasma atomic emission spectrometer with dual scanning monochromators was used. The salient features of the instrument are as follows. The standard equipment for delivery of the sample to the plasma was a cross-flow nebulizer fed by a peristaltic pump and a Scott spray chamber. Both the nebulizer and spray chamber were fabricated from Ryton, a fluorochloro polymer. An alumina injector completed the corrosion-resistant sample introduction system. The two monochromators were evacuated to permit reading in the vacuum ultraviolet region. Monochromator A, which was fitted with a 3600 grooves/mm grating, covered the wavelength region from 160–400 nm and monochromator B, with 1800 grooves/mm, was used for the 160–800 nm range.

Excitation conditions for the analyses are summarized in Table I. To achieve maximum sensitivity for several elements, the source and sample injection parameters were optimized using the optimization routine resident within the Plasma II operating software. The optimized parameters for the emission analysis are those given in Table I.

TABLE I Perkin–Elmer Plasma II instrument parameters
(a) Monochromator parameters

Element	Wavelength (nm)	Viewing height (mm)
Al	396.152	15
Ca	393.366	15
Cu	324.754	15
Fe	238.204	15
Mn	257.610	15
Ti	334.941	15
Y	324.228	6

(b) Source parameters

Parameter	Setting
Power (W)	1200
Pump rate (ml min^{-1})	1.00
Plasma gas (l min^{-1})	15
Auxiliary gas (l min^{-1})	1.0
Nebulizer gas (l min^{-1})	1.250

All element intensities were calculated as a ratio to a scandium internal standard, of which 50 p.p.m. were added to all samples, standards and blanks. Scandium addition was performed immediately prior to analysis to avoid unexpected precipitation of species from the solutions. The scandium internal standard was used as a reference for the Myers–Tracy signal compensation software [2, 3] of the Plasma II. The signal compensation algorithm corrects for long- and short-term drift of such parameters as sample delivery rate and plasma gas fluctuations. The analyte, scandium and argon lines are monitored simultaneously in the Plasma II to provide data for the signal compensation. Some claims have been made that the Myers–Tracy compensation can also correct for differences between the standard and unknown matrices; however, we always attempted to match the matrices of standards and unknowns as closely as possible in order to maximize the accuracy.

2.4. Atomic absorption spectrometry

Chromium and nickel in the samples were determined by atomic absorption to obtain lower detection limits of approximately 5 p.p.m. for each element. This was as much as ten times better than could be achieved by ICP in the sample matrix. The AAS analyses was performed with an Hitachi 180-8 unit.

2.5. Neutron activation

Neutron activation analyses were performed at two university laboratories designated Lab A* and Lab B†. These analyses were purchased on a commercial basis from both facilities. The Lab A experiment irradiated samples for either 30 s or 14 h at $1.5 \times 10^{13}\ n\,cm^{-2}\,s^{-1}$. The decay was monitored for 200–1500 s counts on an Ortec 23% GeLi detector coupled to an ND6700 computerized gamma detection system. At Lab B, for the detection of most elements the samples were irradiated with reactor thermal neutrons while for oxygen and nitrogen fast neutrons were used.

2.6. Preparation of samples by high-pressure HCl–HF dissolution

Portions of hot isostatically pressed bars were cut with a diamond blade wafering saw to yield pieces that weighed approximately 0.2 g. Analytical samples of the pieces were weighed into the Teflon liner of the Parr pressure vessels and heated with a mixture of concentrated hydrochloric and 40% hydrofluoric acids in a 7:3 volume ratio in a Teflon-lined nickel acid-digestion pressure vessel (Parr Model 4747). Samples were heated at 215 °C for 16 h in an air-bath behind a high-pressure barrier. The pressure in the vessel exceeded 2400 ± 1200 MPa (1600 ± 800 lb

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in^{-2}) by extrapolation from low-temperature pressure data in the literature [4]. The Parr vessel was not equipped with any pressure indicators and no experiments were conducted to confirm the estimated pressure.

After the pressure vessel had cooled to room temperature, the clear solution and residual solid were transferred quantitatively to a heavy walled Teflon beaker. To complete the dissolution the sample was treated with 5 ml concentrated sulphuric acid and heated to fuming (approximately 300 °C) on a hot plate in a well-ventilated fume hood.

2.7. Safety considerations

In addition to hazards associated with the use of super-atmospheric pressure, a second safety issue concerning the use of the Parr pressure vessels deserves comment. According to Parr engineers, the design rationale for the Parr acid-digestion pressure vessel is that the Teflon liner "minimizes" contact of the metal and corrosive acid. Nevertheless, under the severe conditions of the dissolutions described above, the nickel body of the vessel was seen to erode with time. The corrosion was evinced by the formation of a water-soluble green solid on the interior vessel walls after each use and a very slow decrease in mass. Although operation with the vessel has continued through many cycles without incident to date, we routinely perform HCl dissolution behind the pressure barrier as a safety measure.

2.8. ICP limits of detection (LOD) and quantification (LOQ)

The limits of detection of the ICP determinations were estimated according to a literature procedure [5] by following the analytical procedure but using the solvent solutions only without any added silicon nitride to obtain "blanks" for the procedure. The LOD was defined as three times the estimated standard deviation (e.s.d.) of the "blanks" for each analyte and the LOQ as ten times the e.s.d. The resulting limits are tabulated in Table II. The corresponding values for the atomic absorption determination of chromium and nickel are also included.

TABLE II ICP limit of detection (LOD) and quantification (LOQ). Method: determine the blank of the analytical method by performing the determination in the empty pressure vessel three times and analysing each effluent for the indicated elements

Define LOD = 3 times the e.s.d. of the blank
Define LOQ = 10 times the e.s.d. of the blank

Element	LOD (mass) (p.p.m.)	LOQ (mass) (p.p.m.)
Mn	1	4
Cu	3.5	15
Ti	1	4.3
Fe	3	14
Y	2	7
Al	0.5	1.5
Ca	1.6	5.5
Cr (AAS)	5	17
Ni (AAS)	5	17

2.9. Scanning transmission electron microscopy

The scanning transmission electron microscopy (STEM) was performed with a Vacuum Generator VG HB5 with a Kevex energy dispersive spectrometer (EDS) attachment. Sample preparation, instrumental parameters, and data reduction were as described by Bradley and Karasek [6]. Sintering aid content was obtained by averaging the analysis from ten fields of view that were 10 μm × 10 μm.

3. Results and discussion

The elemental analytical results from the various techniques studied are summarized in Table III for a set of triplicate analyses of three portions of two samples and in Table IV for single analyses of four additional samples of the silicon nitride.

The repeatability of the determinations can be approximated from the estimated standard deviations of the results. Considerable variability in the precision was observed, depending on the element and on the concentrations in the silicon nitride. However, generally speaking, the ICP–AES and atomic absorption determinations are in good agreement with the STEM results and also with the nominal sintering aid levels. From this we conclude that the acid dissolution process has successfully taken the entire sample into solution. The dissolution included the crystalline β-Si_3N_4, crystalline and non-crystalline grain-boundary phases, as well as intractable impurities such as Fe–Si nitriding agents. In contrast, the neutron activation data are often less precise than the ICP data. This is particularly evident in the case of yttrium, the main sintering aid. The ICP–AES ($5.0 \pm 0.1\%$) and STEM ($5.60 \pm 0.9\%$) data both agree rather well with the nominal value (4.8). The Lab A data ($< 10\%$) were consistent with the AES and STEM analyses as well as the nominal level, but the precision was quite low. Lab B did not even report a yttrium level. We speculate that matrix effects prevented acquisition of adequate neutron activation data.

We anticipate that analogous ICP–AES analyses should be applicable to silicon carbide whisker-toughened silicon nitride as well as composites utilizing other toughening components. However, appropriate conditions for dissolution of samples that contain silicon carbide would be required. Currently the caustic fusion literature techniques for dissolution of silicon carbide [7] also dissolve the platinum or zirconium crucibles commonly utilized for containing the flux.

We speculate that the high-pressure HF/HCl treatment used here for silicon nitride converts the silicon species to silicon fluorides and that fuming reduced the fluoride content. The fuming of the sample following the HF/HCl treatment volatilized silicon tetrafluoride and reduced the fluoride concentration. Failure to reduce the fluoride content sufficiently resulted in incomplete sample dissolution of bulk specimens that contained the sintering aids. In contrast, pure silicon nitride is freely soluble after the high-pressure

TABLE III Elemental composition of isostatically pressed silicon nitride coupons. Mass composition by three techniques[a]

Sample no.	Component (nominal content)	ICP–AES	STEM	Neutron activation	
				Lab A	Lab B
3349-Y-Al	Cr	48 (2.3)[b]	–	51.3 (2.3)	48 (9.5)
	Ni	< 5 (1.0)[b]	–	10.6 (0.8)	10.6 (0.8)
	Mn	10 (1.0)	–	13.7 (0.1)	3.7 (0.4)
	Cu (trace)	1 (0.6)	1	< 30	–
	Ti	39 (1.7)	–	< 250	< 20
	Fe	260 (25)	–	307 (27)	430 (60)
	Y (4.8%)	5.0 (< 0.1)%	5.6 (0.9)%	–	< 10%
	Al (1%)	0.7 (0.1)%	1.2 (0.1)%	–	1.4 (0.05)%
	Ca	950 (26)	1000 (1000)	< 3000	–
20084	Cr	11 (1.5)[b]	–	–	–
	Ni	< 5 (1.0)[b]	–	–	–
	Mn	19 (2)	–	–	–
	Cu	13 (3.6)	–	–	–
	Ti	38 (1.5)	–	–	–
	Fe (0.7%)	0.85 (0.15)%	0.9 (0.1)%	–	–
	Y (3.2%)	3.6 (0.057)%	3.3 (0.5)%	–	–
	Al (0.27%)	0.28 (0.006)%	0.5 (0.1)%	–	–
	Ca	208 (14)	–	–	–

[a] All results in parts per million unless otherwise noted; mean of three separate determinations for AAS, ICP–AES and neutron activation; mean of ten 100 μm^2 fields of view for STEM. The estimated standard deviations are in parentheses.

[b] Atomic absorbance spectroscopy.

TABLE IV Elemental composition of isostatically pressed Si_3N_4 coupons. Composition (by mass) of individual samples[a]. Except as noted, ICP–AES determinations on dissolved samples

Component	Sample			
	3996	3819	3489	20093
Cr[b]	44	38	62	12
Ni[b]	< 5	5	6	10
Fe	306	299	395	0.73%
(STEM)				0.8%
(nominal)				0.7%
Y	4.7%	4.7%	4.7%	3.3%
(STEM)	5.6 (1)%	5.8 (1.1)%	6.0 (1.1)%	2.4 (0.5)%
(Nominal)	4.7	4.8	4.8	3.2
Al	0.67%	0.81%	0.78%	0.34%
(STEM)	0.8 (0.2)%	1.0 (0.2)%	1.0 (0.2)%	0.5 (0.2)%
(Nominal)	0.54%	1.0%	1.0%	0.27%
Ca	0.11%	0.08%	0.12%	None detected
(STEM)	0.3 (0.1)%	0.3 (0.1)%	0.2 ± 0.3%	–

[a] All results in parts per million unless otherwise noted; estimated standard deviations in parentheses.

[b] Atomic absorbance spectroscopy.

hydrofluoric/hydrochloric acid treatment, without addition of sulphuric acid or fuming.

4. Conclusion

We have demonstrated a technique for dissolving densified silicon nitride samples in an aqueous solution based upon a high-pressure HF/HCl treatment. Subsequent analyses of this solution by standard ICP–AES and AAS spectrometries result in determination of sintering aid and impurity levels. Precision is better than that attainable by STEM EDS because STEM requires much smaller sample volumes. Neutron activation experiments generally corroborated our chemical analyses, although we are able to attain more accurate and precise results with the technique described here.

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