Ingeniería, investigación y tecnología
ISSN: 1405-7743
Facultad de Ingeniería, UNAM

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Ingeniería, investigación y tecnología, vol. XX, no. 4, 00012, 2019, October-December
Facultad de Ingeniería, UNAM

DOI: https://doi.org/10.22201/fi.25940732e.2019.20n4.048

Ingeniería Investigación y Tecnología
volumen XX (número 4), octubre-diciembre 2019 1-13
ISSN 2594-0732 FI-UNAM artículo arbitrado
Información del artículo: Recibido: 9 de mayo de 2019, reevaluado: 29 de julio de 2019, aceptado: 15 de agosto de 2019

http://dx.doi.org/10.22201/fi.25940732e.2019.20n4.048

Ingeniería
Investigación y
Tecnología

Determination of fracture toughness and elastic module in materials based silicon nitride

Determinación de la tenacidad de fractura y modulo elástico de materiales a base de nitruro de silicio

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Abstract

The knowledge of the mechanical properties of any material subjected to loads is necessary for its use in structural applications. Silicon nitride (Si_3N_4) ceramics are well-known materials used in engineering applications due to their outstanding combination of high strength and fracture toughness. The most studied mechanical properties of Si_3N_4 are hardness, fracture toughness and mechanical resistance. Recent advances in the production processes that incorporate high purity rare earth elements as sintering additives have improved these mechanical properties. Using Vickers indentation method, the elastic module and fracture toughness of Si_3N_4 based materials modified with La_2O_3, Y_2O_3 and Al_2O_3 were determined as a function of the cracking system type that prevails under the effect of load. The results indicate that adding rare earth to the matrix increased the fracture toughness the Si_3N_4 base ceramic Samples containing La_2O_3+Y_2O_3 showed higher values of fracture toughness than the ones with Al_2O_3+La_2O_3, regardless of the equation used in the calculations. Meanwhile the elastic module decrease approximately 100 GPa for both types of nitrides by the effect of the temperature.
Keywords: Silicon nitride, fracture toughness, hardness, Vickers indentation method.

Resumen

El conocimiento de las propiedades mecánicas de cualquier material de ingeniería es necesario para su uso en aplicaciones estructurales, donde el material se someterá a cargas. Los cerámicos de nitruro de silicio (Si_3N_4) son materiales bien conocidos que se utilizan en aplicaciones de ingeniería debido a su excelente combinación de alta resistencia y resistencia a la fractura. Las propiedades mecánicas más estudiadas del Si_3N_4 son la dureza, la resistencia a la fractura y la resistencia mecánica. Los recientes avances en los procesos de producción que incorporan elementos de tierras raras de alta pureza como aditivos de sinterización han mejorado estas propiedades mecánicas. Usando el método de indentación Vickers se determinaron, el módulo elástico y la resistencia a la fractura de los materiales a base de Si_3N_4 modificados con La_2O_3, Y_2O_3 y Al_2O_3 en función del tipo de sistema de grietas que prevalece bajo el efecto de la carga. Los resultados indican que la adición de tierras raras a la matriz aumentó la tenacidad a la fractura. Las muestras de Si_3N_4 que contienen La_2O_3+Y_2O_3 mostraron valores más altos de tenacidad a la fractura que las que contienen Al_2O_3+La_2O_3, independientemente de la ecuación utilizada en los cálculos. Mientras tanto, el módulo elástico disminuye aproximadamente 100 GPa para ambos tipos de nitruros por el efecto de la temperatura.
Descriptores: Nitruro de silicio, tenacidad de fractura, dureza, método de indentación Vickers.

http://dx.doi.org/10.22201/fi.25940732e.2019.20n4.048

Introduction

Some of the most important engineering ceramics are alumina (Al_2O_3), silicon nitride (Si_3N_4), silicon carbide (SiC) and zirconia (ZrO_2) combined with some other refractory oxides. Of all advanced ceramics, silicon nitride probably has the most useful combination of properties for industrial purposes, such as diesel engine valves, components exposed to thermal shocks, bearings, and other slipping surfaces where they must have good mechanical properties at high temperatures, high hardness, low thermal conductivity and high wear resistance (Matizamhuka, 2018; Richerson, 2012; Schmid, 2002). The possible applications in materials engineering make the development of strategies to obtain these ceramics very broad (Lenoe *et al*., 2013). Ceramic materials, in addition to being very hard and resistant to wear, have good resistance to compressive stress compared to other types of materials; therefore, are ideal for use in bearings. Despite having these characteristics in their favor, the high brittleness and low toughness of these materials was always an obstacle to the mass production of ball bearings; however, in 1972 silicon nitride emerged as the first successful ceramics for the manufacture of high-speed and high-load bearings (Richerson, 2012; Riley, 2000). All the properties of the ceramic materials are affected by the microstructure, therefore, the key to control the performance of a ceramic material is its microstructure during processing, while controlling the morphology and distribution of the microstructural elements (stoichiometry, size, shape and crystalline configuration of the grains, distribution, orientation, arrangement, chemical characteristics of the present phases and their grain boundary) so that the various properties are compatible with the material (Yang *et al*., 2002). The ceramic materials based on silicon nitride are prepared from powders constituted by a phase α which are converted into sintering at phase β. In this way, the final microstructure of these is composed of β-Si_3N_4 phase grains (in many cases totally), and small proportions of α-Si_3N_4 phase grains that do not achieve their transformation (Bellosi & Babini, 1999). This bimodal structure is characterized by the mixing of small and equiaxial grains, corresponding to the α-Si_3N_4 phase, with elongated grains of generally fibrous morphology, belonging to the β-Si_3N_4 phase (Bondanini *et al*., 1999). Among the most relevant points determining the microstructural characteristics of the silicon nitrides are the proportion and the size of the phase a in the starting powders, the temperature and the sintering time, the volume of the liquid phase, the viscosity and the solubility of the nitrogen in the liquid. Sintering additives also play an important role in the final microstructure of silicon nitride materials and it has been found that when they are added in certain percentages the densification increases and the transformation is favored to the phase β-Si_3N_4 which is very important to improve the mechanical properties of the material, especially the fracture toughness (Zhou *et al*., 2006), which is limiting in many of its possible applications in the engineering area due to the brittleness of the ceramic materials, especially in those components subject to cyclic stress loads, however, through some microstructural manipulation mechanisms that have been developed during the last decades, have made it possible to counteract, to some extent, these effects; drastically increasing the fracture toughness of these materials to make them competitive with materials such as foundries (Weimer, 2012). The increasing demand in the use of these new materials warrants having the data necessary to predict its behavior and its useful life under the conditions of service for which its use is projected (Richerson, 2012; Zhou *et al*., 2006). In this way, the tests for determination fracture toughness and its elastic modulus become indispensable to establish the patterns of design and use of these new materials, taking into account that it is necessary to have a greater reliability as well as, a better prediction of the performance of the mechanical components in which they will be used to operate efficiently, even under more severe operating conditions in terms of high temperatures, loads and speeds (Melendez, 2001). The mechanical failure of the ceramic materials is mainly due to structural defects. The main causes of fracture in polycrystalline ceramics are due to surface cracks produced during surface finishing processes, pores, or inclusions produced during processing. In preliminary investigations, it has been determined that materials possessing low toughness tend to develop a system of radial medial crack, whereas materials with high fracture toughness are favored by the *palmqvist* system of cracks (Cook *et al*., 1964). However, recent investigations (Chicot *et al*., 2004) have found that many materials exhibit both cracking systems and that their occurrences will depend on the level of loading applied to the indentation. In this sense, studies by Cook & Braun (1994) and by Kaliszewski *et al*. (1994), indicate that at low loads cracks of the *palmqvist* type are formed and that this morphology changes to *radial medians* when the applied load over-passes a limit load value; this limit value depends on the material being tested, therefore, in addition to the interest of the calculation of the fracture toughness and the elastic modulus of these ceramic materials, will also be verified through this research the system of cracks that predominates when subjected to loads and the effect of the temperature is these properties, it should be noted that these ceramic materials are suitable for selection with other materials such as metal, having as an initial disadvantage its high price. In this sense, the prediction of fracture toughness of these materials becomes a universal challenge crucial for the successful application of new materials in different technologies, a framework in which this research is intended to be introduced.

Experimental

Obtaining samples

The samples used in this study were produced in collaboration with the Institute of Ceramics Research located in Faenza, Italy. Commercial silicon nitride powders (without additives) of brand UBE SNE10®, whose characteristics are presented in Table 1, were used for its manufacture.

From these powders two types of samples were produced, using as sintering additives powders of La_2O_3, Y_2O_3, and Al_2O_3. The proportions of these additives, as well as the compositional characteristics of each type of sample, are presented in Table 2. The selection of these compositions for the manufacture of the samples is based on previous results reported by several researchers for the which have obtained the best microstructure characteristics and the best mechanical properties for these materials (Shaw & Pethica, 1986).

The process of incorporating the sintering additives into the silicon nitride powder (as shown in Figure 1) was done by mechanical mixing of the powders by sti-

Table 1. Characteristics of the silicon nitride powders used to obtain the samples

Characteristics		Powders of Si_3N_4
Specific surface area (s.s.a) [m^2/g]		11.5
Average particle size [μm]		0.19
Average additive size [μm]		0.7
α- Si_3N_4 [Vol %]		95.0
Impurity [wt %]	O	1.4
	Ca	0.005
	Fe	0.010
	Al	0.005
	Cl	0.010
Atomic relation	N/Si	1.0
	Si/O	2.2
	N/O	2.2

Table 2. Identification and composition of the samples

		Samples	
		Si_3N_4-A	Si_3N_4-B
Additives [wt %]		3% La_2O_3+3% Y_2O_3	3% Al_2O_3+8% Y_2O_3
Specific surface area [m^2/g]		12.0	10.3
Impurity [wt %]	O	3.4	-
	N	38.3	-
Atomic relation	Y/Si	0.018	0.16
	La/Si	0.0102	-
	Al/Si	-	0.15

Si_3N_4-A* and Si_3N_4-B* identification the samples with post-heat treatment

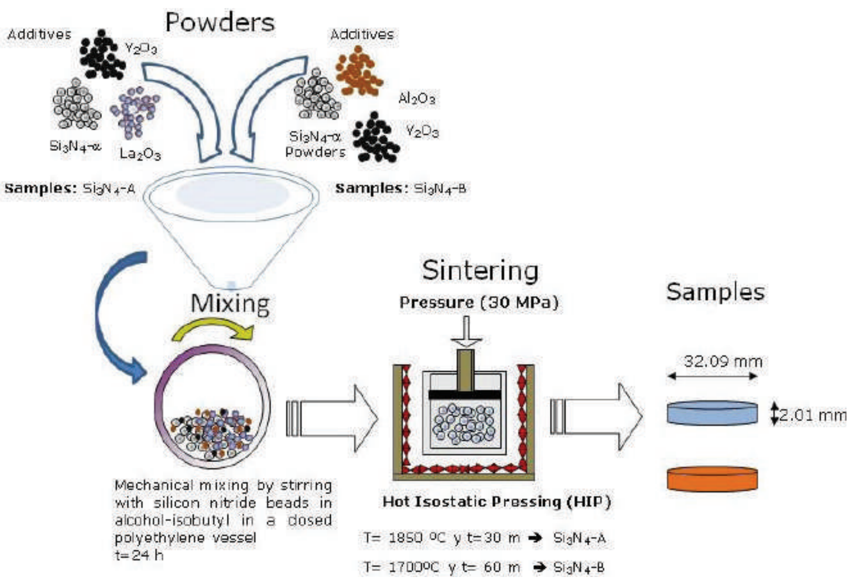

Figure 1. Schematic diagram of silicon nitrides samples fabrication via powder metallurgy method

rring with silicon nitride beads in alcohol-isobutyl in a closed polyethylene vessel for a time of 24 hours. The powder mixtures were densified by hot isostatic pressing to the vacuum, in an induction furnace using a graphite dice at a temperature of 1850 °C, a time of 30 minutes for the samples identified as Si_3N_4-A, and 1700 °C for 60 minutes for the samples identified as Si_3N_4-B, in both cases, a constant pressure of 30 MPa was used.

The conditions of the heating and cooling stages, as well as the time in each of the stages, have been studied previously (Bellosi & Babini, 1999). The manufactured samples have a disk shape with dimensions of 32.09 mm in diameter and 2.01 mm in thickness. The microstructural characterization by Scanning Electron Microscopy and the determination and quantification of the phases by X-ray diffraction for these samples was carried out in a previous work in which the influence of the additives (La_2O_3, Y_2O_3 and Al_2O_3) was evaluated in the microstructure and properties of silicon nitride (Carrasquero *et al*., 2005).

In order to corroborate the results presented by Yang *et al*. (2001), who demonstrated by a comparative study with silicon nitride (with and without subsequent heat treatment) that it is possible to promote the crystallization of phase interactions and the elimination of their stresses, and thus an improvement in the fracture toughness of these materials. In order to evaluate such effect of the temperature on the values of the mechanical properties initially obtained by the sintering process, a heat treatment was carried out after 300 °C to a group of samples in a furnace in an argon atmosphere for a period of 6 hours, subsequently verifying if there were changes in the values of the mechanical properties.

Determination of the elastic modulus (E)

For the measurement of the elastic modulus (E), the instrumented indentation technique was used in a CSEM® brand equipment with a Vickers type pyramidal tip indenter. For the calculation of the elastic modulus, the equipment performed the automatic calculation based on the procedure established by Pharr & Oliver (1992). Five indentations were performed for different charge values from 25 to 300 g. For both types of samples, a Poisson coefficient ν = 0.26 was used, the approximation speed of the tip of the indenter to the surface of the sample was 10 nm/s. The time used in both the loading and unloading process was 10 s and the waiting time after the test load reached

Determination of fracture toughness (K_c)

For the measurement of fracture toughness, the Vickers indentation method was used. Before the indentations were carried out on the samples, the surface preparation of the samples was carried out, which were surface preparation using polishing disks with diamond particles of 120 and 200 µm, followed by a polishing with a suspension of alumina of 1 and 0.3 µm. Six indentations per charge applied to the two types of silicon nitride were carried out using a macro-hardness tester Wollpert universal using loads of 294, 196, 147 and 98 N and a dwell time of 60 s was imposed at the maximum load. The macro-hardness tester was equipped with a Vickers diamond pyramid indenter. Subsequently, the diagonals of the indentation were measured as well as the length of the cracks they generated, with the aid of an optical microscope coupled to an image analyzer. The measurements allowed to calculate the parameters c, a and l shown in Figure 2 and that are used for the calculation of the toughness following the procedure proposed by Ponton & Rawlings, (1989), where the parameter "c", (equals the sum of the average length of the cracks produced under the indentation and half of the average length of the indentation diagonal) must be calculated in both directions of the indent.

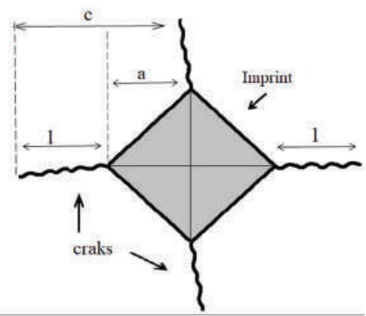

Figure 2. Schematic of the imprint that occurs on the surface of the sample due to the applied load

Determining the system of cracks that occur in the material under the loads being applied is of vital importance since the equations for establishing the value of toughness are related to the type of crack formed. Ponton & Rawlings, (1989), generalized the equations belonging to the groups of the following way:

$$K_{CM} = \alpha \left(\frac{E}{H_v} \right)^q \left(\frac{P}{c^{3/2}} \right) \quad (1)$$

$$K_{CP} = \beta \left(\frac{E}{H_v} \right)^r \left(\frac{P}{a \times l^{1/2}} \right) \quad (2)$$

where:

E and H_V = modulus of elasticity and Vickers hardness of the sample, respectively
P = applied load in the indentation
c, a and l = lengths of the parameters presented in Figure 2
α, β, r and q = parameters that vary according to the author who proposing the equation
M or P in the term K_C = the type of crack system that is formed (M corresponds to the system of median radial cracks and P corresponds to the system of cracks type *palmqvist*

According to Ponton & Rawlings, (1989), the most used equations for the calculation of fracture toughness by the Vickers indentation method are the following:

Equation proposed by Anstis *et al*. (1981):

$$K_{CM} = 0.016 \left(\frac{E}{H_v} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (3)$$

Equation proposed by Evans & Charles (1976):

$$K_{CM} = 0.0824 \left(\frac{P}{c^{3/2}} \right) \quad (4)$$

Equation proposed by Gong *et al*. (2002):

$$K_{CM} = 0.046 (EH_v)^{1/2} \left(\frac{a^2}{c^{3/2}} \right) \quad (5)$$

This three equations assumes as mode of cracking the *median-radial* type if the ratio between the length of the crack to the half of the indent diagonal, $c / a \geq 2$. For the second case, corresponding to the system of cracks type *palmqvist* the equations proposed by Niihara *et al*. (1982) and Shetty *et al*. (1985) which indicate that if $c/a \leq 3$, the characteristic length would be given by the average length of cracks measured from the vertex of the indentation, l, instead of c. Thus, for values of l/a in the range from 0.25 to 2.5, the Niihara & Shetty equations can be expressed as follows, respectively:

$$K_{CP} = 0.00089 \left(\frac{E}{H_v} \right)^{2/5} \left(\frac{P}{\alpha \times l^{1/2}} \right) \quad (6)$$

$$K_{CP} = 0.0319 \left(\frac{P}{\alpha \times l^{1/2}} \right) \quad (7)$$

To determine which expression is the most adequate to perform the calculation of fracture toughness, the criterion established by Chicot *et al.* (2004) was used. These researchers posed the determination of the slope of the line that is obtained by plotting the relation of ln(c/a) *vs*. ln(P). If the slope of the line obtained with the experimental values approaches a value of 1/2, it is estimated that the system of cracks is type *palmqvist,* and if it has a value close to 1/6 the system of cracks that predominates is the radial median type.

Determination of hardness

Measurements were made through a Wollpert durometer, with an attached Vickers indenter, using loads 10, 15, 20 and 30 Kg. For the calculation of the hardness, the following equation was used (Gong, 1999):

$$H_v = 1.854\left(\frac{P}{d^2}\right) \quad (8)$$

where:

H_V = Vickers hardness (MPa)
P = applied load (Kg)
d = arithmetic average of the length of the two diagonals of the imprint (mm)

Results and discussion

Elastic module

The results obtained from the determination of the elastic modulus (E) are shown in Figure 3. It is seen in Figures 3a and 3c that for both types of silicon nitrides there is a similar behavior indicating a decrease of (E) with the indentation load, reaching a constant value of 250 GPa from a load of 3 N. In the literature, values of the elastic modulus ranging from 290-325 GPa for silicon nitride have been reported depending on the composition, processing and the method of measurement used (De Pablos *et al*., 2003). For example, for the same composition of the Si_3N_4-A samples, (Bondanini *et al*., 2001) obtained a value of the elastic modulus of 325 GPa using the ultrasound resonance technique, this value is higher than that obtained by microindentation. However, by using the procedure established by Pharr & Oliver, (1992), more discrete values of the elastic modulus

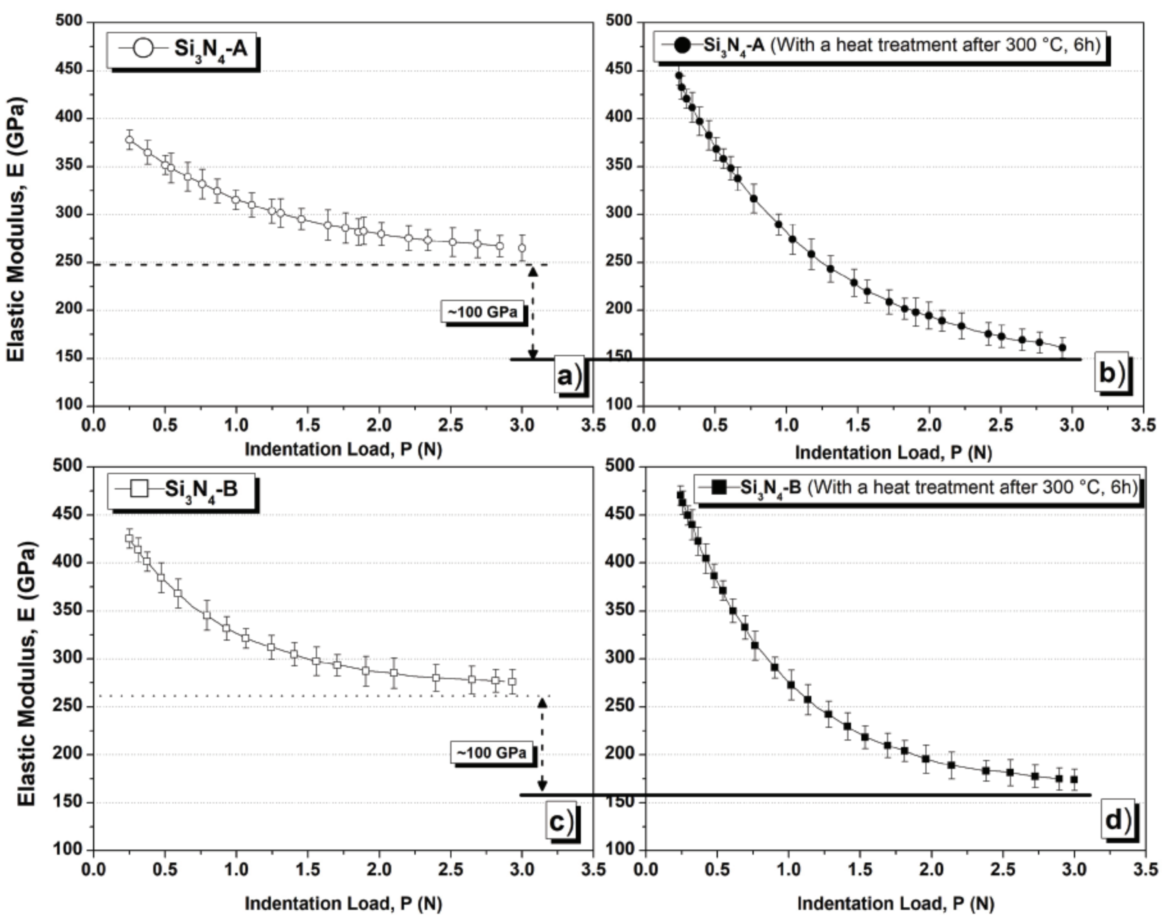

Figure 3. Variation of the elastic modulus with respect to the indentation load, a) sample Si_3N_4-A; b) sample Si_3N_4-A with a heat treatment after 300 °C, 6 h; c) sample Si_3N_4-B; d) sample Si_3N_4-B with a heat treatment after 300 °C, 6 h

are guaranteed as a function of the set of phases present in the microstructure compared to the general value that is obtained when using the ultrasound technique. After the thermal treatment of the samples, the elastic modulus was measured again to evaluate if the samples underwent any change of this property due to the temperature effect (Figures 3b and 3d); even though the elastic modulus decreases with respect to the indentation load, there is a decrease in its value of approximately 100 GPa for both kinds of nitrides, being 150 GPa from the load of 3 N. It is evident that effectively the value of the elastic modulus has been influenced by the increase of the temperature, due to the diffusion mechanisms as reported by Yang *et al*. (2000) that the use of subsequent thermal treatments promotes the crystallization of larger quantities of refractory phases in the grain boundaries of β-Si_3N_4 phase, thus reducing the residual stresses produced by the sintering process.

For the determination of the fracture toughness of the samples, the value of the elastic modulus of 250 GPa was considered for both types of nitrides in initial condition and 150 GPa for the samples that were submitted to the heat treatment after 300 °C by 6 h .

Fracture Toughness (Kc)

Figures 4 and 5 show the variation of the fracture toughness (K_c) with the indentation load for each of the equations presented in the literature both types of samples, with and without post-heat treatment.

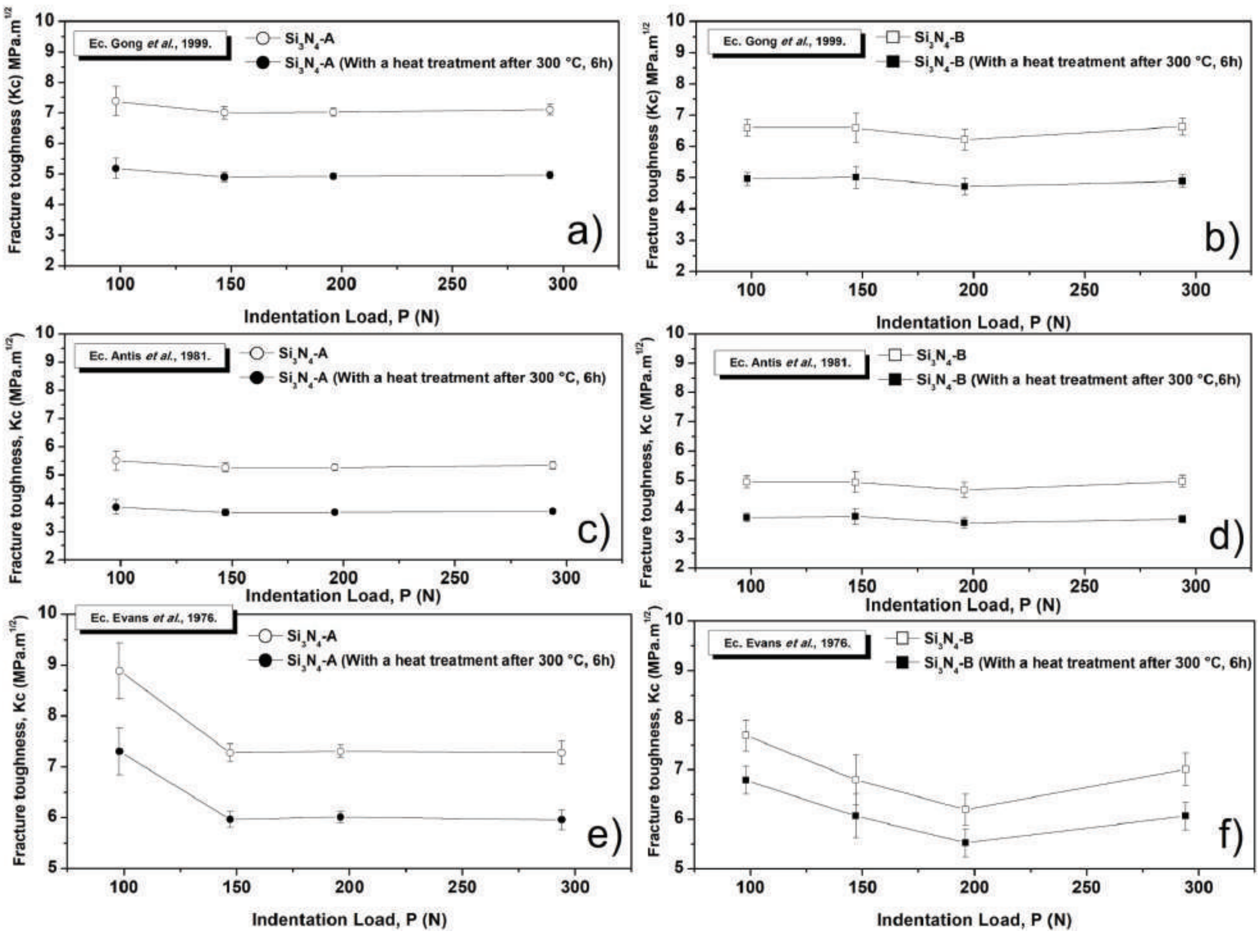

Figure 4. Fracture toughness values (K_c) for radial median cracks system: a) and b): using the Eq. Gong *et al*. (1999); c) and d): using the Eq. Anstis *et al*. (1981); e) and f): using the Eq. de Evans *et al*. (1976)

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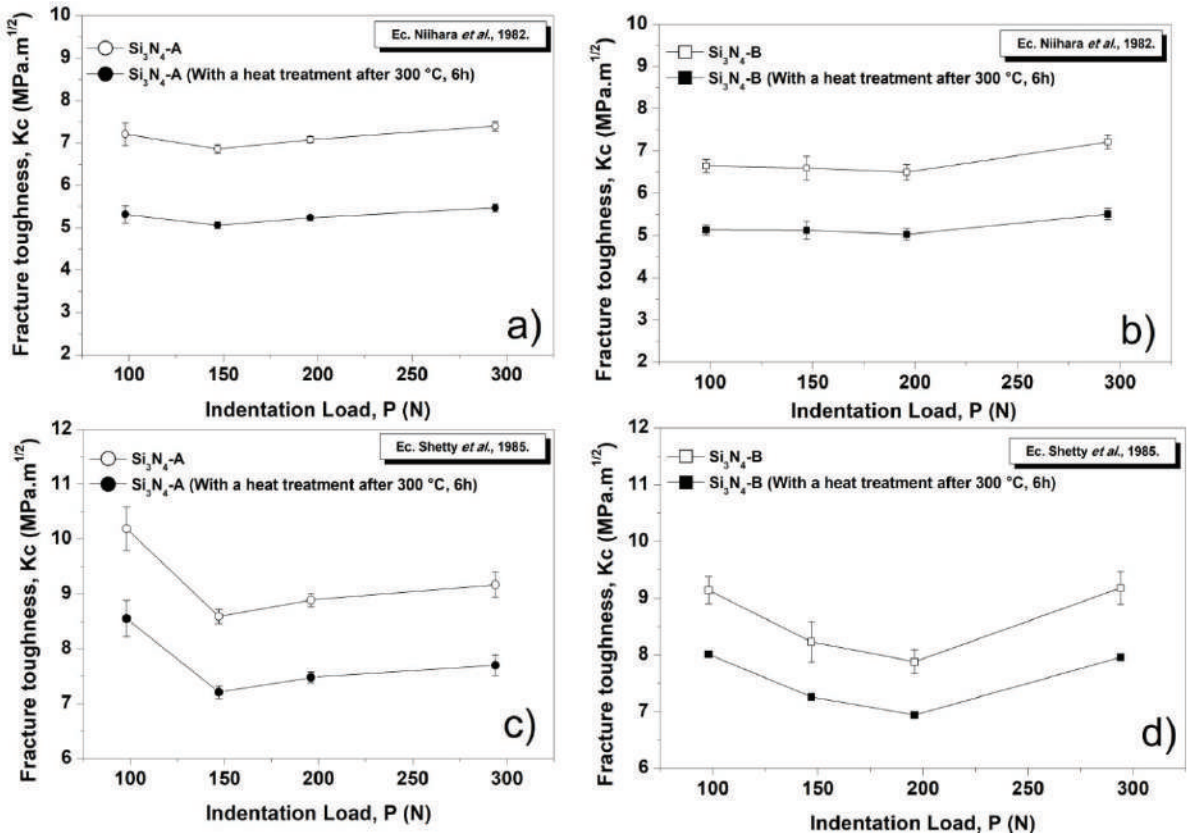

Figure 5. Fracture toughness values (K_c) for system of cracks type palmqvist, a) and b) using the Eq. de Niihara *et al*. (1982); c) and d) using the Eq. Shetty *et al*. (1982)

With these results, the method proposed by Chicot *et al*. (2004), to know in advance which crack system predominates in the load range used and to know which equations represent the most reliable values. For this, we calculated the slope of the line obtained by plotting the relation of ln(c/a) vs. ln(P). In Figure 6, these relations and their respective equations of the lines obtained by the linear regression method of the experimental data are represented.

The slopes of the lines for Si_3N_4-A and Si_3N_4-B (Figure 6) have an approximate value of 0.14 and 0.15 for both types of nitrides and with a heat treatment after 300 °C, respectively; all the slopes of the lines are closer to the value of 1/6 than the value of 1/2 , so it is concluded that the silicon nitride develops predominantly in the load range under study a system of radial cracks for both compositions and regardless of whether they have undergone changes or not by the effect of temperature Chicot *et al*. (2004). It should be noted that this same system of cracks coincides with the results of the work done by researchers (Lube, 2002; Miyazaki *et al*., 2010; Ordoñez, 2013), who reported that from the 98 N of applied load on the indentation the radial median crack system for this type of ceramic material is developed. Once it was known which crack system predominated, it was analyzed which of the equations formulated for this type of system, represents the best results of fracture toughness in comparison to those reported in the literature. Using the equation proposed by Evans *et al.* (4), slightly higher fracture toughness values were recorded for Si_3N_4-A than Si_3N_4-B, however, among the samples that suffered the effect of temperature (Si_3N_4-A* and Si_3N_4-B*), the toughness values are very similar, with a reduction of approximately 22 % and 13 % with respect to the initial samples. For any of the cases, the values of the use of this expression are higher in comparison with those obtained using the equation of Anstis *et al.* (3), since it is not considered term of the relationship between the elastic modulus and the hardness of the material for the calculation of the fracture toughness. The results obtained using the equation proposed by Anstis *et al.* The highest values of K_c correspond to Si_3N_4-A with respect to Si_3N_4-B, even for those that suffered the effect of temperature.

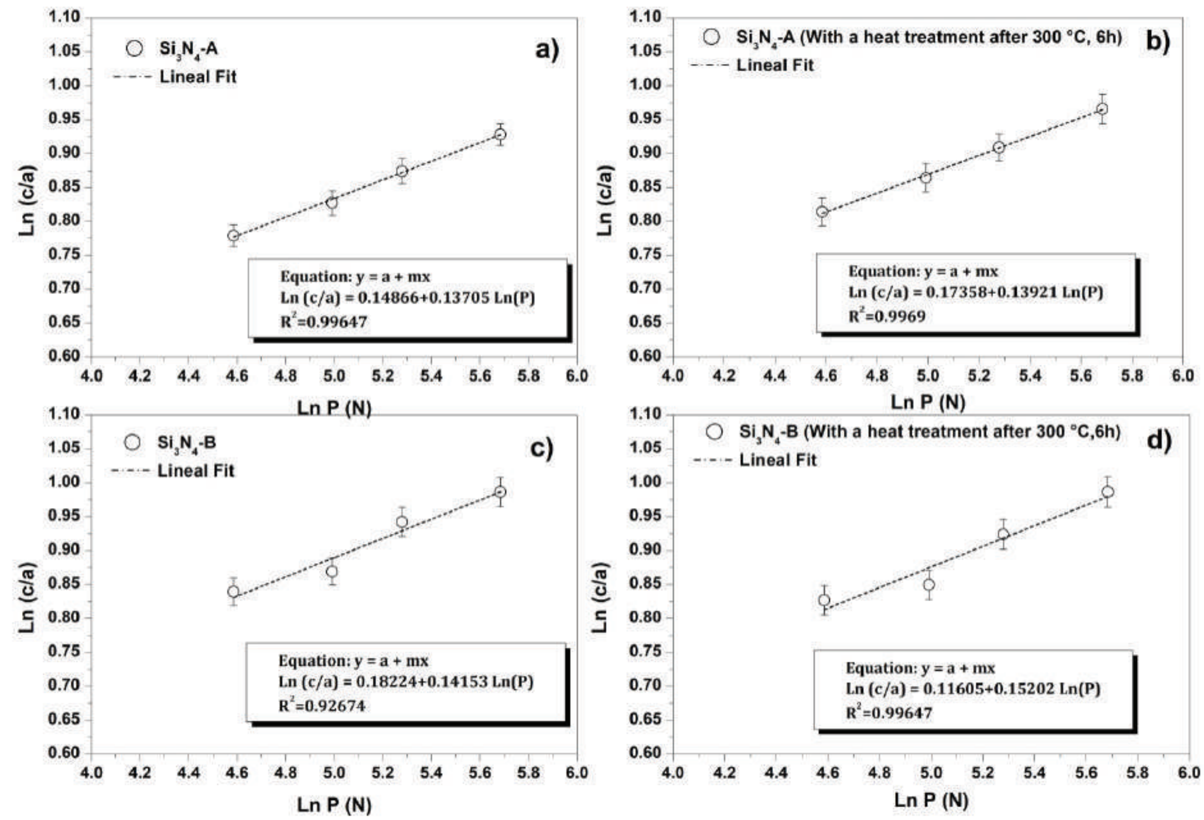

Figure 6. Determination of the crack system: a) sample Si_3N_4-A; b) sample Si_3N_4-A with a heat treatment after 300 °C, 6 h; c) sample Si_3N_4-B; d) sample Si_3N_4-B with a heat treatment after 300 °C 6 h

In contrast to the results obtained by the Evans equation (4), it can be observed that the values of K_c practically remain constant with respect to the applied load, due to the fact that in this case, if the value of the elastic modulus and the hardness of the material for the load used. The effect of the temperature on the fracture toughness generated a reduction of the K_c value in the order of 43 % and 23 % for Si_3N_4-A and Si_3N_4-B, respectively.

Evaluating the results obtained using the equation proposed by Gong *et al*. (5), as in the previous case, the highest values of K_c correspond to Si_3N_4-A. Very similar values of K_c are obtained for the samples that underwent the effect of temperature. However, when using this equation, a decrease in fracture toughness value of 43 % and 33 % was recorded for the Si_3N_4-A* and B* samples, respectively. Comparing the values obtained by using the equation of Anstis *et al.* (1), This expression proposed by Gong (1999) which is a modification Lawn *et al*. (1980), who considered the use of the apparent hardness of the material, while Gong *et al*. (2002), used an empirical expression for obtaining the real hardness, independent of the geometry of the indenter and the way the load is applied, however, it is not taken into account the elastic constants of the material, the friction effect in the contact and how the material flows under the indenter. It is important to take into account at the time of the determination of K_c by the Vickers indentation method the effect of the change of hardness with the applied load or better known in the literature as the *effect of the size of the indentation* in the hardness (*ISE*), this effect generates a problem in the selection of the load to be used to obtain a correct K_c value, this is because the equations used are deduced from values of constant hardness, thus introducing systematic errors in the calculation of K_c.

Hardnees

Figure 7 shows how the hardness with respect to the applied load varied for the four samples under study. The hardness of the Si_3N_4 varies with the load until reaching a constant value, obtaining for both types of nitrides a value of approximately 18 GPa, whereas for

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samples Si_3N_4-A* and B* this value is close to 15 and 14 GPa, respectively. These results agree with those presented in the research carried out by Bellosi & Babini, (1999), which reported hardness values for silicon nitrides measured under Vickers microindentation at a load of 9.81 N, values of 18.6 ± 0.3 GPa for Si_3N_4-A and 17.3 ± 0.4 GPa for Si_3N_4-B. As can be seen in Figure 7, there is a small difference between the samples and that they are closely linked to their compositions which, as already mentioned, is responsible for the final microstructural characteristics of the material and, therefore, the mechanical properties they exhibit.

These results are corroborated to those reported by Zutshi *et al.* (1994), who evaluated the Vickers hardness variations in different types of silicon nitride, finding that they are associated to any changes related to the composition of the grains and morphology. In order to calculate the fracture toughness of all the samples studied, the load at which the hardness reached a constant value (P ≥ 147 N) was taken into account and also ensured that the cracking produced was not excessive or to produce non-uniform tracks as recorded at the maximum load (P = 294 N). With the use of P ≥ 147 N the best results are obtained in the fracture toughness measurements in this type of material since from this load it was obtained that the parameter $P/c^{3/2}$ remained constant verifying the review (Lube, 2002).

Generally and independently of the equation used for the determination of K_c, the highest values corresponded to Si_3N_4-A and Si_3N_4-A* in comparison to the other two respective samples. From the microstructural point of view, these results are in agreement with the literature for this type of material, since there is a well-defined relationship between microstructure and fracture toughness as a function of how it interacts with cracks through the mechanisms of deflection, separation of grains and branching of cracks and where there are two key parameters in the microstructure that give indications of how they act as it is size and shape relationship of the β-Si_3N_4 phase. The effect of grain size on the toughness has already been studied by others (Matsuhiro &Takahashi, 2008), who reported that the polycrystalline Si_3N_4 with the same relation of form, the samples that had a bigger grain size presented a greater

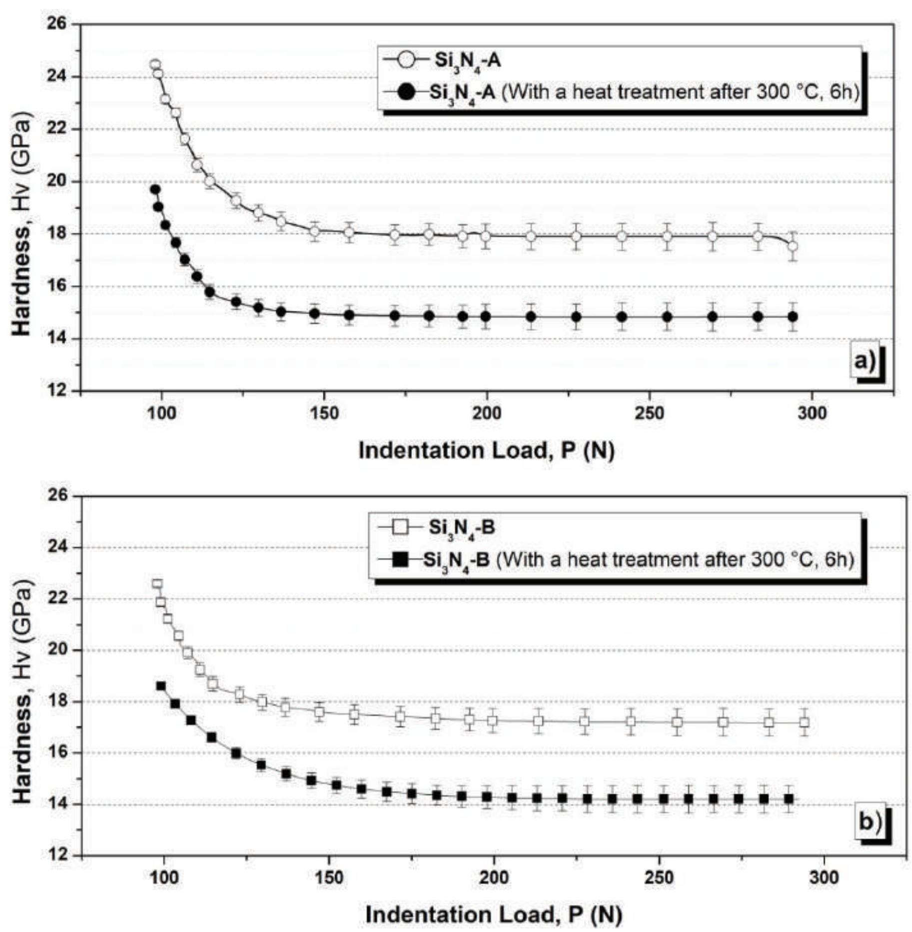

Figure 7. Variation of the hardness with respect to the applied load in the indentation: a) sample Si_3N_4-A with and without post-heat treatment; b) sample Si_3N_4-B with and without post-heat treatment

resistance to the propagation of cracks, often occurring deviations around large grains and dispersions of energy in the generation of secondary cracks. With regard to the shape relationship of the β-Si_3N_4 phase grains as it increases, the deflection mechanisms and crack bridges are more effective (Ordoñez, 2013). A previous investigation carried out for the same nitride composition (Carrasquero *et al*., 2005); where Si_3N_4-A presented interlaced elongated phase grains (β-Si_3N_4) with values of shape and grain size much lower than with respect to Si_3N_4-B and that the amount of residual α-Si_3N_4 phases was 13.77 % and 28.28 % for Si_3N_4-A and Si_3N_4-B, respectively.

These previous results explain the reason why the highest values K_c corresponded to Si_3N_4-A and Si_3N_4-A* in comparison to the other two Si_3N_4-B and Si_3N_4-B*, since the Si_3N_4-A has a higher value of grain shape ratio, fundamental parameter for the activation of the crack deflection mechanism, also contains a lower percentage of residual α- Si_3N_4 phase, as reported by De Pablos *et al*. (2003), where a lower content of this phase in the microstructure generates an increase in fracture toughness. An analysis of which of the three equations proposed in the literature for the *radial median* crack system (3, 4 and 5) express the closest toughness values to those obtained using conventional tests for determination of K_c of the silicon nitride manufactured under different methods reported in the literature is presented in Table 3.

Comparing the results obtained from the use of the three equations for the determination of fracture toughness for the *radial medial* crack system, we can show that equation of Anstis *et al.* (3) is the one that yields results comparable to the values reported in the literature by other writers, for similar compositions and microstructures, since they were obtained with the application of this equation values average K_c of 5.29 ± 0.13 $MPa.m^{1/2}$ and 4.86 ± 0.27 $MPa.m^{1/2}$ for Si_3N_4-A and Si_3N_4-B, respectively.

It should be pointed out that with the use of the Vickers indentation method for the calculation of fracture toughness (K_c) values very close to those of K_{IC} can be obtained, with accuracy close to 30 % with respect to those reported in the literature (Ponton & Rawlings, 1989).

Table 3. Fracture toughness values reported in the literature

Reference	Composition Samples	Technique used	Fracture toughness K_{IC} ($MPa.m^{1/2}$)
(Ordoñez, 2013)	Si_3N_4 + 6 % Y_2O_3 + 4 % Al_2O_3	CNB*	5.60
	Si_3N_4 + 6 % Y_2O_3 + 4 % MgO	CNB	5.20
(Zutshi *et al*., 1994)	Si_3N_4 + 2 % Y_2O_3 + 5 % Al_2O_3	Indentation	5.45
(Gong *et al*., 2002)	Si_3N_4	SEPB**	6.10
(Melandri *et al*., 1995)	Si_3N_4+ 3 % Al_2O_3 + 8 % Y_2O_3	Indentation	4.80
(Wang & Mao, 1995)	Si_3N_4+ 5 % Al_2O_3 +2.5 % Y_2O_3 + 7.5 % La_2O_3	CNB	8.06
(Kim *et al*., 1989)	Si_3N_4+ 3 % Al_2O_3 + 8 % Y_2O_3	Indentation	4.66
(Bellosi & Babini, 1999)	Si_3N_4 + 3 % La_2O_3 +3 %Y_2O_3	Indentation	4.70-5.90
	Si_3N_4+ 3 % Al_2O_3 +8 % Y_2O_3	Indentation	4.80-5.50
(Liang *et al*., 1999)	Si_3N_4 + 6 % Y_2O_3 + 2 % Al_2O_3	Indentation	5.08-6.35
(Lu & Huang, 2001)	Si_3N_4 + 6 % Yb_2O_3 + 2 % Al_2O_3	SEPB	11.80
	Si_3N_4 + 6 % Y_2O_3 y 2 % Al_2O_3	SEPB	6.20

* Chevron-Notched Beam (CNB), ** Single-Edge Precracked Beam (SEPB)

Conclusions

From the results presented in this work, it is concluded that in general and independently of the equation used for the determination by indentation of fracture toughness, the highest values corresponded to the silicon nitride samples modified with La_2O_3 and Y_2O_3 as compared to those modified with Al_2O_3 and La_2O_3, attributed to the microstructural characteristics generated by these sintering additives, which produced a self reinforced structure with a larger grain size and radius of appearance of the grains of the phase-β that favor the increase of the resistance to the fracture. A decrease of the elastic modulus in its value of approximately 100 GPa for both types of nitrides was also corroborated by the effect of the temperature at which the samples were subjected during the heat treatment after 300 °C, final value obtained is within the average values reported for these ceramic materials above 150 GPa. The use of the expression proposed by Anstis *et al.* (1981) is the one that yields comparable results to the values reported in the literature by other authors, for similar compositions and microstructures. By means of the indentation technique, the intrinsic fracture toughness of the material can easily and quickly be obtained without the need for more sophisticated and cumbersome methods, where larger samples and more complex geometries are required.

Therefore, the evaluation of the mechanical properties of the silicon nitride samples modified with La_2O_3+Y_2O_3 such, elastic modulus and fracture toughness indicates that the additions of rare earth gives rise to a significant improvement of the mechanical performance. Therefore, the outcome derived from the evaluation of the mechanical properties of the ceramic under study allow an explanation of the results previously reported in the literature concerning the improvement of the engineering ceramic.

Acknowledgments

To the National Fund for Science, Technology and Innovation (FONACIT) through the UCV Project S1-2002000475 for the funding received and the Research Institute for Ceramics Technology (Faenza, Italy) for their collaboration in the preparation of the samples.

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