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Indentation strength of silicon nitride ceramics processed by spark plasma sintering technique

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ABSTRACT

We investigated the influence of the microstructure on the true stress–strain curve of silicon nitride based ceramics. The materials were processed by spark plasma sintering technique. Si_3N_4 with fine, average and coarse microstructures were obtained. Load versus displacement curves (P–h) were obtained by means of instrumented indentation technique using diamond coni-spherical tip. The experimental data were coupled with a minimization method based on the Levenberg–Marquardt algorithm and the non-linear part of the mechanical response was identified. Based on the obtained stress–strain curves, rolling contact simulations were performed. In addition, the nature of Hertzian contact damage was examined in the material with coarse microstructure using diamond indenters of radii 0.2 and 1 mm. The surface damage was observed under optical microscopy while Focused Ion Beam Sectioning technique permitted to image the subsurface damage. An evident size effect was noticed: fracture consisting of classical ring cracks dominated at large scale while distributed microcracks beneath the indent dominated at small scale.

1. Introduction

Silicon nitride based ceramics exhibit a remarkable combination of mechanical properties: good wear, oxidation and corrosive resistance [1], low density (3.2 g/cm^3), excellent thermal shock resistance, resistance to impacts, high hardness (1600–2000 Hv) [2] and one of the highest fracture toughness among ceramic materials (6–10 MPa m$^{1/2}$) [3]. Therefore, silicon nitride based materials have been widely used in various industrial domains since 1950s. For example, Kristic [4] mentioned applications in nuclear fusion reactors, construction of thermal conductors and gas turbines. Hampshire [5] cited structural application at high temperatures in turbocharger rotors while Bal and Rahaman [6] reported recent clinical use of silicon nitride to promote bone fusion in spinal surgery and current developments as femoral heads for hip joints. Today, rolling bearing manufacturing companies are increasingly turning to Si_3N_4 with a growth of about 40% per year [7], high-pressure turbopumps on NASA space shuttles are a representative example [8].

Si_3N_4 exists in two[1] major crystallographic structures: trigonal α metastable form at low temperatures and hexagonal more stable β form. Idealized α and β forms are assigned to space groups P31c and P6$_3/m$, respectively [10]. An irreversible $\alpha \rightarrow \beta$ phase transformation occurs above 1400 °C leading to β elongated grains and to the so-called *in situ* composites or self-reinforced materials exhibiting a higher fracture toughness [1]. Because of its high boundary energy and low diffusivity coefficient, sintering of fully dense Si_3N_4 by means of conventional or unconventional techniques requires an addition of small amounts of various additives (MgO, Al_2O_3,Yb_2O_3, La_2 O_3, etc.) [11–13]. During the sintering process, the additives react with the silicon nitride and the silica present at surface of each single powder to form an intergranular glassy film. This phase is few nanometres thick, it enhances precipitation and rearrangement mechanisms needed to achieve full densification but strongly impacts the mechanical and thermal behaviour of ceramic materials at room and elevated temperatures [14–17]. Depending on the application target, the quantity of sintering additive and processing conditions can be controlled to obtain tailored microstructures with small equiaxed or large elongated grains [18]. In coarse microstructures, grains with high aspect ratio enhance the toughening mechanisms such as crack bridging, deflection and grain pull-out which is found to significantly improve the fracture toughness value and the overall crack resistance [14,3,19–21].

The Hertzian damage is a crucial issue in the lifetime

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[1] A third phase, cubic Si_3N_4 was synthesized under high conditions of temperature and pressure [9].

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estimation of brittle materials, especially for application in rolling bearings. Previous studies in hot-pressed dense silicon nitride revealed a significant influence of grain size on the contact damage mechanisms [22]. In fact, a transition from brittle mode to quasi-ductile mode was experimentally demonstrated when grain size increases. The first mode consists of ring cracks created during loading by the radial stress which is maximum (tensile) at the surface along the contact area boundary, whereas the second mode is shear and compression-driven damage beneath the indent [23,24]. However, all these studies have not taken into account the motion of the rolling body, which radically changes the stress fields and consequently the subsurface damage.

To assess the local mechanical behaviour of a large variety of materials including hard technical ceramics, instrumented indentation technique is generally used [25–28]. An indenter of a given geometry is pushed into a flat well-polished surface. The applied load, P, and the vertical displacement of the indenter, h, are simultaneously recorded during testing to obtain a P–h curve. Oliver and Pharr method [29] improved the earlier work of Doerner and Nix [30] to capture Young's modulus and hardness from the unloading part of the measured curves assumed to be purely elastic.

The plastic properties of ductile materials can also be derived from the load versus displacement curves. The usual procedure consists of coupling analytical formulas with finite element simulations to derive required mechanical parameters. Based on a rigorous dimensional analysis, Dao et al. [31] proposed a set of dimensionless functions to calculate the plastic parameters of various pure and alloyed engineering metals with isotropic hardening from instrumented indentation with Vickers and Berkovich tips. The set of functions was afterwards extended by Chollacoop et al. [32] to other indenter tip geometries (50°, 60°, 80° cones) and Bucaille et al. [33] to take into account the friction coefficient in the identification process. Based on this approach, isotropic [31], anisotropic [34] and viscoplastic [35] constitutive laws were successfully identified.

Regarding brittle hard materials, a different approach is generally considered to characterize the non-linear behaviour: a spherical indenter with a radius, R, mounted on a standard tensile machine is pressed on the polished surface of the specimen. Afterwards, the contact radius of the permanent indent, a, is measured under optical or Nomarski microscopy after gold coating. The indentation stress or mean pressure, p_0, is defined as the maximum applied load, P, divided by the contact area after complete unloading, *i.e.* $p_0 = P/\pi a^2$, and the indentation strain, a/R, as the contact radius a divided by the sphere radius R [36]. In the elastic domain, p_0 is proportional to a/R [37].

Using a set of indenters with various radii, a scatter-plot is obtained and $p_0(a/R)$ relations are then used to derive the mechanical behaviour of the brittle materials. Fischer-Cripps and Lawn [38] analysed the stress field in tough ceramics and proposed simple relations based on finite element calculations to determine the work hardening coefficient α (α ranges between 0 and 1: 0 for perfect plasticity without hardening and 1 for pure elasticity). In this approach, the yield stress Y corresponding to the first plastic flow is experimentally determined. Indeed, by combining the critical shear stress criterion and Hertzian theory, it is possible to correlate the yield stress Y with the mean pressure of subsurface damage initiation. From the micromechanics point of view, it is found that Y is related to the intrinsic shear stress of the different materials while α is determined by the damage intensity Nl^3 where N is the density and l the size of the faults [39].

However, for hard materials such as Si_3N_4, the deviation from linearity in the indentation stress–strain curve is overestimated because of the flattening of the indenting spheres [22]. In fact, it is found that the yield stress and hardening coefficient of Tungsten carbide (WC) indenters are below the identified values of tested specimens. In addition, the described technique requires optical measurements of the remaining contact radius and subsurface damage observation increasing the uncertainty of parameter values.

Alternative methods taking advantage of the recent development of high precision indentation instruments are then needed. In this context, an approach was recently proposed by Luo et al. [40] to calculate the true σ–ϵ curve of Si_2N_2O–Si_3N_4 composites based on nanoindentation tests using a Berkovich rounded tip and FEM calculations. Because of the size of the indenter considered by the authors, $R_{berk} \simeq 500$ nm, only ultra-fine-grained microstructures were tested. Other approaches based on TEM nanoindentation of ceramic nanoparticles [41] or nanocubes [42] and compression of micropillars [43] were also proposed. But in each case, a sophisticated *in situ* nanomechanical testing system is required and the derivation of behaviour laws at larger scale, relevant for macroscopic products, has not been addressed yet.

The purpose of the present work on silicon nitride based materials is twofold: (i) to use instrumented indentation testing with single spherical indenter available commercially and inverse identification to obtain the true stress–strain relations. (ii) To investigate the size effect on the nature of Hertzian contact damage mechanisms of silicon nitride ceramics with coarse microstructure under indentation. Numerical simulations using in-house software were then performed to simulate the development of this damaged zone under pure rolling loading.

2. Materials and techniques

2.1. Material elaboration

A commercial nanosized Si_3N_4 powder (SN-ESP, UBE Industries, Japan) with high α/β ratio (≥ 95%) was used as a starting material. Powders with high α-phase content are known to lead to materials with better mechanical properties thanks to the β elongated grains resulting from the phase transformation at high temperatures [44]. Physical properties of SN-ESP powder are summarized in Table 1. Various amounts of yttrium oxide (Y_2O_3, 99.99% high purity, Wako Pure Chemical Industries, Japan) ranging from 1% to 5% were added to the starting silicon nitride powder in order to obtain different microstructures (from fine to coarse). The powder mixtures were ball milled in ethanol with alumina balls as grinding media and finally dried in an electric oven at 80 °C.

The samples were sintered into disks of diameter 30 mm and thickness 3 mm in nitrogen (N_2) gas atmosphere using spark plasma technique (SPS 1050, Syntex Inc., Japan). The technique has the capability to densify the starting powders in a drastically shorter time and at lower temperature than other conventional processes. Heating rates during sintering were as follows: 120 °C/min from 0 to 600 °C, 100 °C/min from 600 °C to 1600 °C, then 20 °C/min from 1600 °C to 1700 °C. This latter one is held constant for 15 min. The applied mechanical pressure was in all cases of 40 MPa. All the materials and corresponding processing conditions are listed in Table 2.

Table 1
Physical properties of starting silicon nitride SN-ESP powder.

Grade SN-ESP	**SSA** (BET) 6–8 m^2/g	**Density** ($g\,cm^{-3}$) 3.19
Purity	O ≤ 2.0%	C ≤ 0.2%, Cl ≤ 100 ppm
	Cl ≤ 100 ppm	Fe ≤ 100 ppm, Al, Ca ≤ 50 ppm
Phase	α-Phase crystal ≥ 95%	