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Effects of oxidation on surface stresses and mechanical properties of liquid phase pressureless-sintered SiC–AlN–Y_2O_3 ceramics

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Abstract

The understanding of the oxidation mechanism of 50 wt% SiC–50 wt% AlN composites obtained by means of pressureless sintering without the protective powder bed and with Y_2O_3 as sintering-aid were significantly improved by means of Raman spectroscopy. These analyses put in evidence that "amorphous carbon" started to be formed at 1300 °C as main effect of active oxidation of SiC. At higher temperature the crystallization process began and it was completed at 1500 °C when only graphite could be recognized. On the basis of these new evidences, oxidation effects on the mechanical properties of SiC–AlN–Y_2O_3 composites were defined. First of all, heat treatment in air was able to induce a compressive surface stress due to the volume gain associated to the oxidation of the intergranular phase. As a consequence apparent fracture toughness showed a value of 6.6 MPa $m^{1/2}$ after a heat treatment at 1300 °C, while at higher temperature effects of active oxidation caused a decreasing up to 4.7 MPa $m^{1/2}$. This toughening mechanism was also used to improve the resistance to thermal shock, which was evaluated by performing quenching tests. Furthermore, passive oxidation induced the healing of superficial flaws by means of the formation of α-cristobalite. This phenomenon was assumed to be responsible for the increasing of the flexural strength.

Keywords: Silicon carbide; Aluminum nitride; Mechanical properties; Composite; Residual stress; Raman spectroscopy

1. Introduction

Silicon carbide (SiC) and aluminum nitride (AlN) form a 2H solid solution, which has received considerable attention owing to its high potential for application in chemically aggressive environments [1,2]. The SiC–AlN composites were sintered by hot pressing [3–5], gas-pressure sintering (GPS) [6], pressureless sintering with liquid phase forming additives (LPS) [7–9] and they were extensively characterized in order to establish the correlation between mechanical properties (toughness and flexural strength) and microstructural features [10–13]. Moreover, we reported in previous papers that 50 wt% SiC–50 wt% AlN composites could also be pressureless sintered in absence of the powder bed normally used to reduce the weight loss associated to the sintering process [14,15]. Furthermore this material showed high toughness and improved high temperature mechanical properties with respect to liquid phase pressureless-sintered SiC–Al_2O_3–Y_2O_3 system [16] resulting very promising for advanced structural applications at high temperature.

In addition, oxidation behavior is an important feature, which has to be assessed in order to evaluate the potential applications of these materials at high temperature. Oxidation rates of composites with different SiC/AlN ratio were previously determined by different authors [17–19]. In the case of 50 wt% SiC–50 wt% AlN ceramics, it was already demonstrated that pressureless-sintered composites with Y_2O_3 as sintering aid showed a high oxidation resistance up to 1400 °C, due to the formation of a protective oxide scale composed by mullite, cristobalite and yttrium disilicate [15]. On the contrary, the same material exhibited a different behavior at 1500 °C leading to the formation of large pores in the oxide scale. As possible explanation of this phenomenon, a mechanism based on the change from passive to active oxidation of SiC at 1500 °C was proposed, but a better understanding of the intermediate stages of the oxidation mechanism is necessary to improve the mechanical properties of this material. Raman spectroscopy, normally used for residual stresses determination [20,21], was used in this work to analyse oxidized samples with the aim to investigate the intermediate stages which

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Table 1
Characteristics of the starting powders

Powder	Purity (wt%)	Specific surface area (m^2/g)	Particle size (μm)
α-SiC	>97.0	15.6	0.48
AlN	>97.0	3.6	0.1–0.5
Y_2O_3	99.9		

occurred during the transition from passive to active oxidation of SiC. The additional information extracted from Raman analysis were consequently used to study how the oxidation mechanism influences mechanical properties in order to establish the best pre-oxidation treatment necessary to improve the performance at high temperature of this material.

2. Experimental procedure

Commercially available α-SiC (UF10, H.C.Starck, Germany), AlN (Pyrofine A, Atochem, France) and Y_2O_3 (H.C.Starck, Germany) were used as starting powders with a weight ratio of 48:48:4. The characteristics of these powders are reported in Table 1. Forming and sintering procedures have been already described in detail elsewhere [14]. Rectangular pellets (11 mm × 12 mm × 8 mm) were prepared from the bulk specimen with a diamond saw. Oxidation experiments were carried out at different temperatures in the range 1200–1500 °C over a period of 1 h in air [15].

Raman spectra were collected using the spectrometer Renishaw System 1000, with excitation from an Ar^+ laser at the wavelength of 514.5 nm and with a spectral resolution of 3 cm^{-1}. The incoming power was reduced with a neutral filter whose optical density was selected in each experiment to prevent thermal effects in the sample, the actual power focused on the sample never exceeding 2 mW [22]. The point to point variation of the Raman spectra, from the surface oxide scale to the bulk of the samples, was obtained by moving the sample with an x–y motorized stage of a microscope (Olympus BX40) interfaced to the spectrometer. By using a 50× objective, a spatial resolution of 0.85 μm, with a theoretical field depth of about 25 μm, was reached.

Mechanical properties (fracture toughness and thermal shock resistance) were determined before and after oxidation. Fracture toughness was determined on the polished samples surface by means of Vickers indentation method with indentation load in the range 49–196 N (five samples for each load) [23]. Polishing procedure in the oxidized samples ensured that oxidation layer was greatly removed and that Vickers indentations were consequently performed underneath the oxidation layer.

Finally, thermal shock resistance was determined by water quenching method in according to the standard EN 820-3.

3. Results and discussion

3.1. Raman spectroscopy analysis

The main difference between passive and active SiC oxidation is the formation of carbon (graphite) in the active oxidation instead of silica according to these reactions [24,25]:

$$SiC_{(s)} + 3/2O_{2(g)} \Leftrightarrow SiO_{2(s)} + CO_{(g)} \quad (1)$$

$$SiC_{(s)} + O_{2(g)} \Leftrightarrow SiO_{(g)} + CO_{(g)} \quad (2)$$

Reaction (1) is referred to the passive oxidation, while the active oxidation mechanism is based on reaction (2). The main difference between these two mechanisms is that passive oxidation leads to the formation of silica, whereas the active oxidation produces gaseous species (SiO and CO) that cause rupture of the oxide scale [15]. In the latter case, silica and graphite are also produced as intermediate reaction products on the basis of the following reactions:

$$SiC_{(s)} + O_{2(g)} \Leftrightarrow SiO_{2(s)} + C_{(s)} \quad (3)$$

$$SiO_{2(s)} + C_{(s)} \Leftrightarrow SiO_{(g)} + CO_{(g)} \quad (4)$$

Therefore, identification of the graphite in the oxide scale is necessary for the discrimination between these two different oxidation mechanisms and consequently a better understanding of the high temperature behavior of the material.

A previous study conducted by Xu and Zangvil [26] on the oxidation mechanism of hot-pressed SiC–AlN ceramics revealed the formation of SiAlON and graphite as oxidation products at 1400 °C. These experimental evidences were extracted after SEM, TEM and HREM analysis. It is interesting to note that these authors confirmed that it was very difficult (and expensive) to obtain TEM thin foils from SiC–AlN sintered samples and consequently only few samples could be examined.

On the contrary, Raman spectroscopy could be easily used to examine SiC–AlN ceramics, since the sample preparation is very simple and at the same time it is well known that it is a powerful tool for the “in situ” characterization of the different forms of elemental carbon [27].

The carbon atom has four valence orbitals, which can hybridize to form sp^2 and sp^3 orbital combinations. The sp^2 orbital forms planar structures with threefold symmetry at the carbon atom and is found in aromatic molecules and in crystalline graphite. The sp^3 orbital forms the basis for three dimensional, tetrahedrally bonded carbon as in methane (CH_4) and in diamond. The most well known forms of elemental carbon found in nature are graphite and diamond. Diamond spectra are characterized by a Raman band at 1332 cm^{-1}, while graphite shows a first order phonon at about 1580 cm^{-1}; both bands are fairly sharp. When the long-range order of the graphite lattice is disrupted, new and broader bands appear, which are usually labeled D-band (∼1355 cm^{-1}) and G-band (∼1590 cm^{-1}). The latter bands are also most commonly referred to as “amorphous carbon” [22,27].

On the basis of this potentiality for the discrimination of different types of carbon, Raman spectroscopy has been widely used for the characterization of carbon-contained ceramics. In particular it was applied in the characterization of SiC fibers to put in evidence carbon impurity and to evaluate residual stresses [28–30]. In fact, when carbon is present as an impurity in a SiC matrix, it is well detectable, due to its scattering cross-section larger than that of SiC, which leads to very strong