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SiAlON ceramics from preceramic polymers and nano-sized fillers: Application in ceramic joining

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Abstract

Commercial polysiloxanes filled with alumina nano-particles have been employed for the preparation of β-SiAlON-based ceramics in the temperature range 1450–1550 °C in nitrogen atmosphere. The formation of β-SiAlON was found to be preceded by the formation of intermediate alumino-silicate phases. The SiAlON yield was affected by the occurrence of phase separation in the oxycarbide ceramic residue (SiOC) derived from the silicones and by the partial vaporization of silica, by reduction into gaseous SiO, leading to products with an oxide contamination, consisting of corundum. Filled silicones finally found a promising application in the ceramic joining, sandwiched between two pre-existing α–β (Yb-)SiAlON pieces and treated at high temperature (1550 °C): with a proper formulation, a significant inter-diffusion was observed between the joining layer and the SiAlON parts, causing the evolution of a homogeneous joint region, matching the microstructure and the mechanical properties of the parent ceramics. The pre-oxidation of the SiAlON, generally aiding the wetting of the joining media prior to thermal treatment, showed no significant benefit on the microstructure. On the contrary, the addition of a small load during the thermal treatment allowed the formation of strong joints, not exhibiting any significant difference in mechanical properties with the parent material.

Keywords: Precursors; Nanocomposites; SiAlON; Structural applications

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1. Introduction

Preceramic polymers have attracted a considerable interest as precursors for advanced ceramic components, mainly due to the processing opportunities given by the viscous flow in the polymeric state, e.g. in the realization of complex shapes or in the manufacturing of ceramic matrix composites, by the infiltration of a preceramic polymer between ceramic fibres, or by the sealing of the residual porosity after sintering.[1–4] However, it must remembered that in the pyrolysis of preceramic polymers the remarkable shrinkage (about 60 vol%) and the formation of cracks deriving from the gas release occurring during the polymer-to-ceramic conversion are poorly controllable.[5,6] Unmodified polymers are consequently most suited for thin-walled components, like fibres,[7] microtubes[8] or foams[9]; monolithic samples may be achieved only by the introduction of appropriate fillers, following the pioneering research carried by Greil.[10] “Active fillers”, consisting of metal (or intermetallic) particles, may react, upon pyrolysis in inert atmosphere, with the gaseous decomposition products coming off the preceramic polymer or with the pyrolysis gas, to yield mainly carbide or nitride ceramics. The volume expansion associated to the conversion of metal particles into ceramics limits both the formation of defects and the shrinkage. An alternative is represented by “passive fillers”, i.e. inert filler powders (in particular SiC or Si_3N_4), which do not react with the preceramic but simply reduce the total shrinkage in the component by diluting the transforming mass.[11]

Recent papers have highlighted a new concept of active fillers, mainly consisting of highly reactive nano-sized oxide powders, such as γ-Al_2O_3 or CaO nano-particles, in combination with commercial polymethylsiloxanes (“silicones”), aimed at the development of important engineering ceramics, such as mullite, wollastonite and SiAlON.[12–16] In these cases the whole ceramic residue deriving from the pyrolysis of the polysiloxanes is intended to react with the fillers. In particular, the synthesis of mullite from a preceramic polymer containing nano-sized fillers,

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for treatments in air, appears promising as it shows a simple and fast route to obtaining components from ceramics which possess a poor solid state sinterability (due to the slow interdiffusion of the components). Mullite is an important intermediate phase, together with sillimanite, also for treatments in nitrogen, being reduced and nitrided to β-SiAlON, with the help of the carbon fraction of the ceramic residue of the polymer, available in a non-oxidative atmosphere.[15,16]

The structural joining of pre-formed components constitutes a promising way for obtaining advanced ceramic articles with complex shapes or with relevant dimensions. Also in this particular field, the preceramic polymers may exploit their intrinsic "dual behaviour". In fact, at room or moderate temperature they can be used, dissolved in a solvent or in the molten state, as a "glue" for pre-formed components, like many ordinary polymers. Upon pyrolysis at high temperatures (typically >1000 °C) the weak bonding available after solidification is transformed into a strong ceramic bonding, due to the conversion of the polymer into a ceramic.[5] The preceramic polymers may allow a certain tailoring to the chemical composition of the ceramic to be joined or infiltrated; as an example, polycarbosilanes, well known as precursors for SiC fibres, may be employed for SiC-based materials.[4,17] A slight chemical mismatch may be admitted: as an example, silicones, yielding a silicon oxycarbide (SiOC) ceramic, were successfully employed for the joining of SiC.[18]

In the present paper we illustrate a combination of the approaches of "nano-filling" and joining via preceramic polymers, applied to the bonding of pre-existing SiAlON pieces. SiAlON ceramics possess a chemical composition which is hardly matched by preceramic polymers. Polysilazanes, well known precursors for Si_3N_4, structurally similar to SiAlON, are quite unstable for the processing of joints (as an example, they may partially decompose by reaction with moisture). The above presented silicones, being more stable, may constitute valid joining materials, if modified with Al. A recent paper, as an example, showed the feasibility of bulk SiAlONs prepared by the addition of polymer derived SiAlOC glass (in turn due to the modification of a silicone polymer with alumatrane)[19]; the present paper, however, is concerned with the modification of silicone resins by addition of alumina nano-particles. Unlike in previous experiments[15,16] SiAlON will be developed from mixtures without secondary additives (Si_3N_4, AlN), thus simplifying the formulation of joining media. It will be shown that the phase compatibility between joining media and ceramic pieces to be joined favours the formation of strong joints, around which the mechanical properties are not significantly altered.

2. Experimental

A commercial α–β Yb-SiAlON ceramic (TK4, 60% $\alpha\text{-}Yb_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where $x \sim 0.29$, 40% $\beta\text{-}Si_{6-z}Al_zO_zN_{8-z}$ with $z \sim 0.44$, Kennametal Inc., Latrobe, PA), fabricated by pressureless sintering, followed by final densification via hot isostatic pressing (density = 3.4 g/cm^3), constituted the reference material. It was provided in the form of bars of approximate dimensions of 5.5 mm × 19.9 mm × 40.4 mm. The bars were cut into smaller samples (about 5.5 mm × 10 mm × 10 mm) by means of a diamond wafering blade (G0597 Surface Grinder, Grizzly Industrial Inc., Bellingham, WA); the sample surfaces were smoothed and polished by means of abrasive platens and clothes soaked with polycrystalline diamond suspensions, up to a finish of 1 μm (see Fig. 1a). Some specimens were subjected to an oxidative pre-treatment at 1300 °C in air for 3 h (with heating and cooling rate of 2 °C/min – see Fig. 1b).

The formulation of the joining media used was 0.3 g of SR355 silicone resin (General Electric Silicone Products Division, Waterford, NY), 0.44 g of pre-dispersed NanoDur^{TM} (Alfa Aesar, Ward Hill, MA) δ/γ-alumina nano-particles (40–50 nm, 50%, w/w) in 50 ml of ethanol. The polymer was first dissolved in ethanol and magnetically stirred for 1 h, then added with the alumina suspension (introduced drop wise) and finally left under magnetic stirring for 24 h. Using an airbrush, approximately 1 ml (52 mg) of the joining media was applied to each face of the samples to be joined (Fig. 1c and d), subsequently overlapped obtaining a sandwich structure. The joints were dried for 12 h at 100 °C (Fig. 1e), in order to remove the solvent and induce flow in the polymer (its T_g is slightly below 100 °C). The samples were then treated in a mildly reducing nitrogen atmosphere (98% N_2/2% H_2, with a flow rate of about 2 cm^3/s) at 1550 °C, for 3 h. Selected samples were subjected to treatment at 1570 °C. The heating rate was 10 °C/min up to 600 °C, then it was set at 2 °C/min; the reverse of this heating cycle was used upon cooling. Selected joints were treated wedged in a graphite fixture (see Fig. 1f): the thermal expansion mismatch between graphite and SiAlON applied pressure to the joint region on heating.

For comparison purposes, 0.44 g of $\gamma\text{-}Al_2O_3$ nano-powders ("aluminium oxide C", Degussa, 15 nm mean particle size) were cast in a solution of 0.3 g of H44 silicone resin (Wacker-Chemie GmbH, München, Germany) in isopropyl alcohol. The mixture was first ultrasonicated for 10 min then poured in a glass container and dried at 60 °C overnight. After solvent evaporation, the mixture was finely ground (into particles < 10 μm) and fired again in a mildly reducing nitrogen atmosphere, at 1450 °C and 1550 °C, with a heating rate of 10 °C/min and a holding time of 3 h. X-ray diffraction analyses (Bruker D8 Advance, Karlsruhe, Germany) were performed on powdered samples, employing Cu Kα radiation (0.15418 nm). The diffraction patterns were analysed by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA).

After thermal treatment the joined samples, mounted in epoxy resin, were sectioned perpendicular to the joint on a low speed saw (Isomet, Buehler Ltd., Lake Bluff, IL). After hand polishing on clothes, using diamond pastes ranging from 74 μm down to 1 μm, the samples were analysed by means of optical microscopy (Olympus BX60M, Center Valley, PA, equipped with a CCD camera) and environmental scanning microscopy (ESEM, FEI Quanta 200, Hillsboro, OR, equipped with EDS attachment). A micro-indentation analysis was performed in the joint region (V-10-C1 indenter, Leco Co. Leco St. Joseph, MI), along a line perpendicular to the same joint: Vickers indents

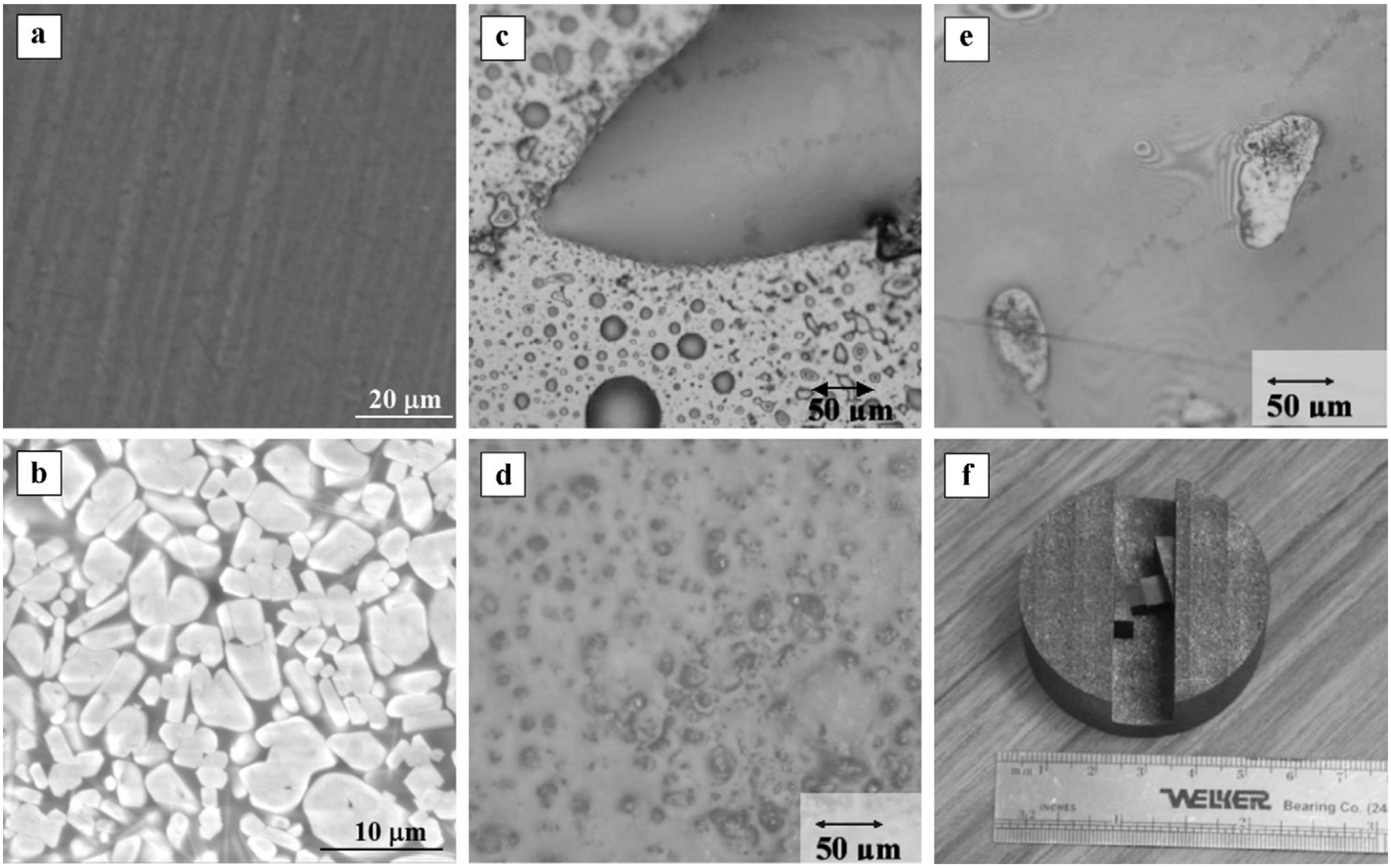

Fig. 1. Details of the preparation of joints: (a) polished SiAlON surface; (b) oxidised SiAlON surface; (c) wetting on un-oxidised surface; (d) wetting on oxidised surface; (e) wetting after drying at 100 °C; and (f) graphite fixture.

yielded the hardness, H_V, with a load of 20 N (applied for 15 s), and the indentation fracture toughness, K_{IC}, at a load of 50 N (applied for 25 s). The fracture toughness was calculated using the equation of Anstis et al.,[20] based on the length of cracks emanating from the corners of Vickers indents. For selected samples also nano-indentation analysis (Hysitron triboindenter with a 500 nm nominal radius conospherical diamond indenter tip, Minneapolis, MN) was applied, along three rows perpendicular to the joint, at a distance of 25 μm from each other. The loading rate was 100 μN/s to a maximum load of 7500 μN with a hold time of 30 s. The unloading rate was 100 μN/s.

Hardness was calculated by dividing the applied load by the contact area A_c, in turn calculated (by means of Matlab) from calibrated area function[21]; the reduced elastic modulus, E^*, was calculated using the equation $E^* = 0.5 \cdot dP/dh \cdot (\pi/A_c)^{0.5}$, where dP/dh is the slope of the unloading curve.[21]

3. Results and discussion

As shown by Fig. 1c, a significant de-wetting of joining media occurs on un-oxidised SiAlON surfaces. Fig. 1d demonstrates that the oxidative pre-treatment undoubtedly improved the homogeneity of the deposition. However, Fig. 1e illustrates that inducing flow in the polymer, at 100 °C, greatly improves the homogeneity even on un-oxidised surfaces (the de-wetting regions are much smaller). This point could be seen as a further evidence of the “flexibility” of preceramic polymers.

The application of load on heating appears essential for the formation of a robust joint. As shown by Fig. 2a and b, the joints without applied load exhibited many discontinuities. Preoxidation of the SiAlON marginally influenced the microstructural evolution (Fig. 2b). Joints fabricated with applied load exhibited a dramatically enhanced microstructural evolution: as illustrated by Fig. 2c and d, the joints have very similar microstructure to that of the parent SiAlON ceramic, and are apparently not affected by the preoxidation treatment. The identification of the joint region was possible only by observing offsets in the sandwich structure (see lower part of Fig. 2d).

Although the optical micrographs did not show significant differences in joints fabricated from un-oxidised or oxidised surfaces, scanning electron microscopy revealed a substantial chemical segregation within the joint. The preoxidation resulted in a alumino-silicate region, partially depleted from high Z-contrast elements, i.e. ytterbium, as shown by Fig. 2f. Un-oxidised surfaces led to joints with very limited modifications, compared to the parent ceramic (Fig. 2e). It must be observed that the joint is very thin (<2 μm).

The formation of a homogenous bonding is likely attributable to the particular “chemical balance” in the joining media. The starting silicone/alumina ratio (3:2.2) corresponds to a silicone solution with a low alumina loading; silicone-based

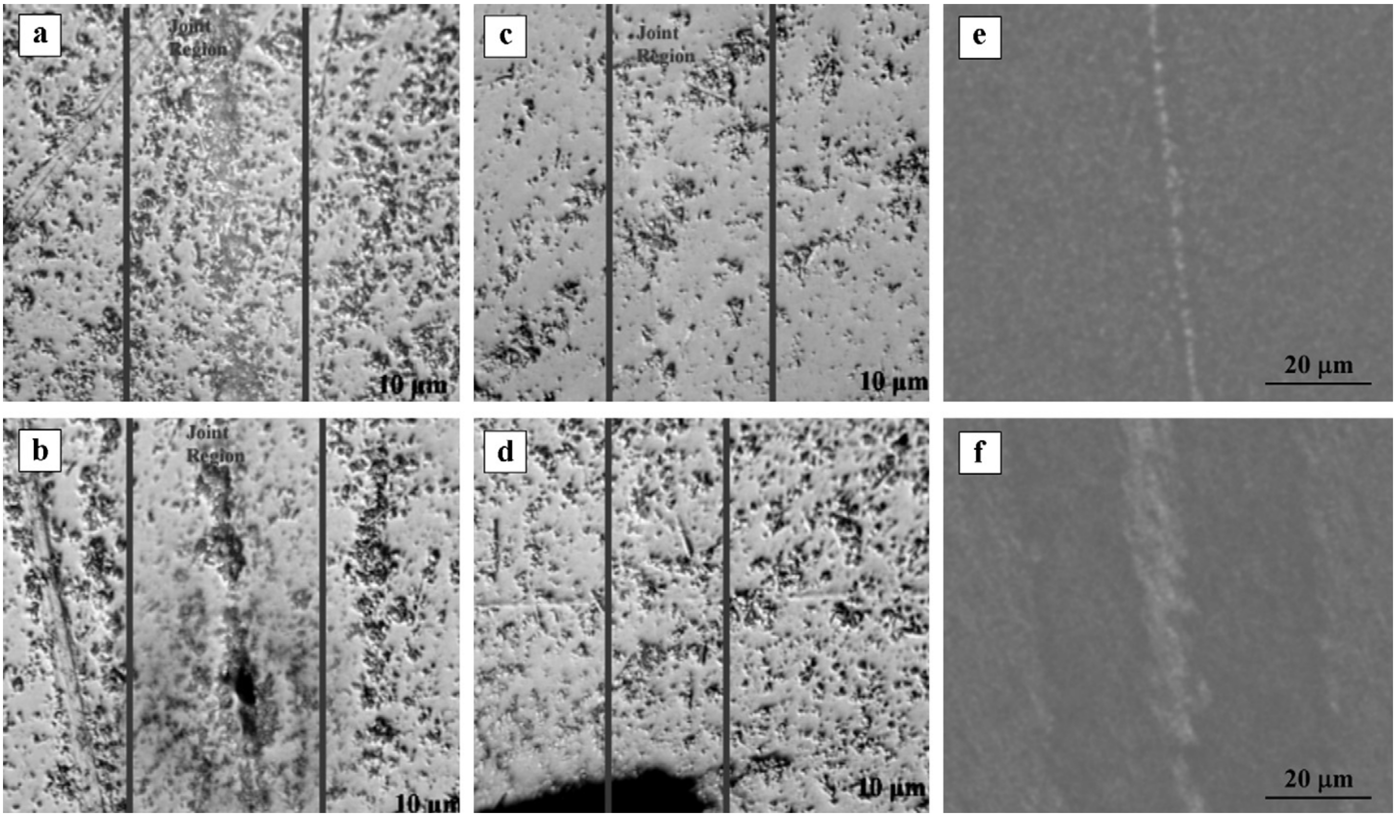

Fig. 2. Joints made without an applied load: (a) un-oxidised; (b) oxidised; joints made with an applied load: (c and e) un-oxidised; (d and f) oxidised [a–d: optical micrographs; e and f: ESEM-EDS microprobe ytterbium maps].

mixtures employed in the past for yielding β-SiAlON,[15,16] in fact, feature an excessive amount of fillers for keeping a significant flow ability (essential, as above reported, for a homogeneous coating of the substrate). The past experiences revealed that β-SiAlON formation, from filled silicones, is preceded by the formation of alumino-silicates (mullite and sillimanite).[15,16] Alumino-silicates were attributed to the reaction of alumina or AlN filler with the silica provided by the phase separation of the SiOC originated by the silicone, yielding also some SiC and C ($SiOC \rightarrow SiO_2 + SiC + C$).[15] The employed silicone/alumina ratio was conceived on the basis of the likely composition of the SiOC from the selected polymer ($Si_3O_{4.6}C_{8.45}$) and the products of phase separation ($Si_3O_{4.6}C_{8.45} \rightarrow 2.3SiO_2 + 0.7SiC + 7.75C$).[22] By assuming that only the silica fraction reacts with alumina, yielding sillimanite ($Al_2O_3{\cdot}SiO_2$), we obtain the following equation (Eq. (1)):

$$Si_3O_{4.6}C_{8.45} + 2.3Al_2O_3 \rightarrow Al_2O_3{\cdot}SiO_2 + 0.7SiC + 7.75C \tag{1}$$

Most of the carbon from phase separation should help the subsequent nitridation of sillimanite to β-SiAlON, as follows:

$$Al_2O_3{\cdot}SiO_2 + 6.9C + 2.3N_2 \rightarrow 1.15Si_2Al_4O_4N_4 + 6.9CO \tag{2}$$

The "global" equation is:

$$Si_3O_{4.6}C_{8.45} + 2.3Al_2O_3 + 2.3N_2 \rightarrow 1.15Si_2Al_4O_4N_4 + 0.69CO + 0.7SiC + 0.85C \tag{3}$$

The newly developed β-SiAlON should correspond to the "joining ceramic". Carbon traces, found in the EDS spectra, are reasonably attributable to the expected SiC and C.

Fig. 3 is the proof that the actual phase evolution is quite more complicated than expected. The figure refers to a mixture comprising H44 polymer and γ-Al_2O_3 nano-powders, treated in mildly reducing atmosphere in the form of powders. The polymer, although of different commercial origin, is chemically analogous to SR355,[23] and the filler is a transition alumina phase, analogous to that used in the joining media. β-SiAlON ($Si_2Al_4O_4N_4$, PDF#76-0598) effectively developed at 1550 °C, together with a remarkable corundum contamination (α-Al_2O_3, PDF#88-0826). Traces of an alumino-silicate phase are also visible, at 1550 °C; the lower part of Fig. 3 shows that this alumino-silicate phase was dominant for treatments at low temperature, i.e. at 1450 °C. Due to the partial overlapping of diffraction peaks, the expected sillimanite ($Al_2O_3{\cdot}SiO_2$, PDF#74-0274) and mullite ($3Al_2O_3{\cdot}2SiO_2$, PDF#79-1275) are hardly distinguishable; according to the semi-automatic phase quantification (based on the relative intensity of main diffraction peaks) provided by the Match! software, mullite and sillimanite should be in a weight ratio of 3:2. A reasonable cause for the

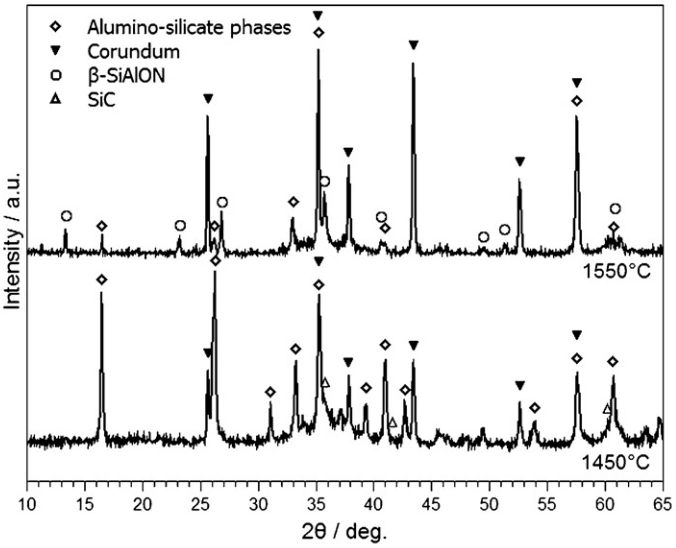

Fig. 3. XRD diffraction pattern of a H44 silicone/Al_2O_3 nano-powder mixture fired at 1450 and 1550 °C in 98% N_2/2% H_2 atmosphere.

development of mullite, i.e. an alumino-silicate phase richer in alumina than sillimanite corundum phase is the volatilization of silica, by formation of SiO gas, in turn due to reactions involving the SiC product of SiOC phase separation, as an example[24]:

$$2SiO_2 + SiC \rightarrow 3SiO + CO \tag{4}$$

Traces of SiC (PDF#73-1708) are effectively present at 1450 °C, as shown by Fig. 3. Intensive silica volatilization may be also a cause for the presence of corundum at 1450 °C, from unreacted γ-Al_2O_3 nano-powders. It should be noted, interestingly, that corundum increases, with the formation of SiAlON and the notable decrease in intensity of peaks associated to alumino-silicates, at 1550 °C. This phenomenology could be interpreted, as in previous investigations,[15,16] with the reduction and nitridation of mullite, as follows[25]:

$$3Al_2O_3{\cdot}2SiO_2 + 6C + 2N_2 \rightarrow Si_2Al_4O_4N_4 + 6CO + Al_2O_3 \tag{5}$$

In practice, the excess of alumina incorporated in mullite instead of sillimanite, at 1450 °C, is removed at 1550 °C.

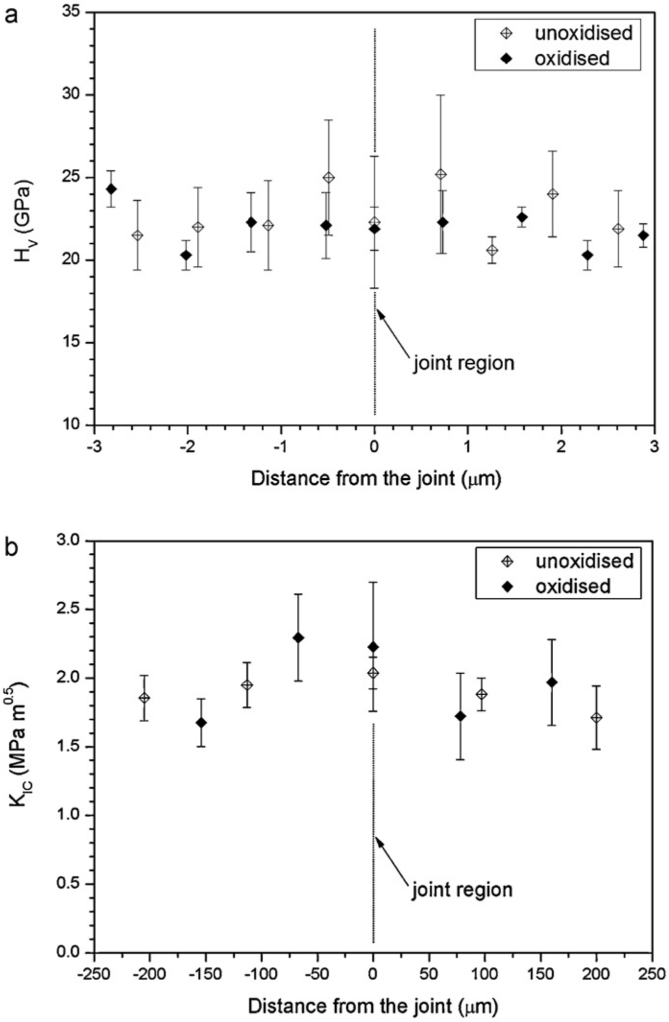

Fig. 5. Plots of Vickers hardness (a) and KIC (b), obtained by micro-indentation, versus the distance from the joint.

The volatilization of silica is likely more favoured for fine powders, representing an “open system”, than for the joint material, not completely surrounded by the atmosphere, being comprised between solid SiAlON pieces. In addition, it should be observed that the β-phase in the SiAlON pieces is relatively poor in Al and O, as inferred from the low *z* value, so that “extra”

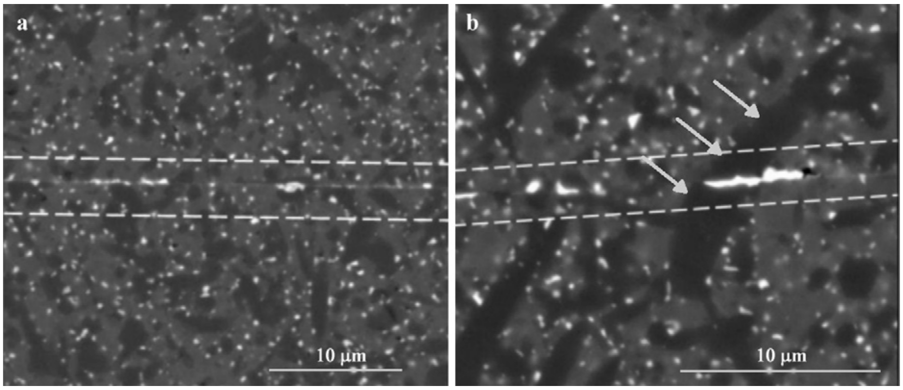

Fig. 4. Backscattered electron SEM images of joints after firing at 1550 (a) and 1570 °C (b).

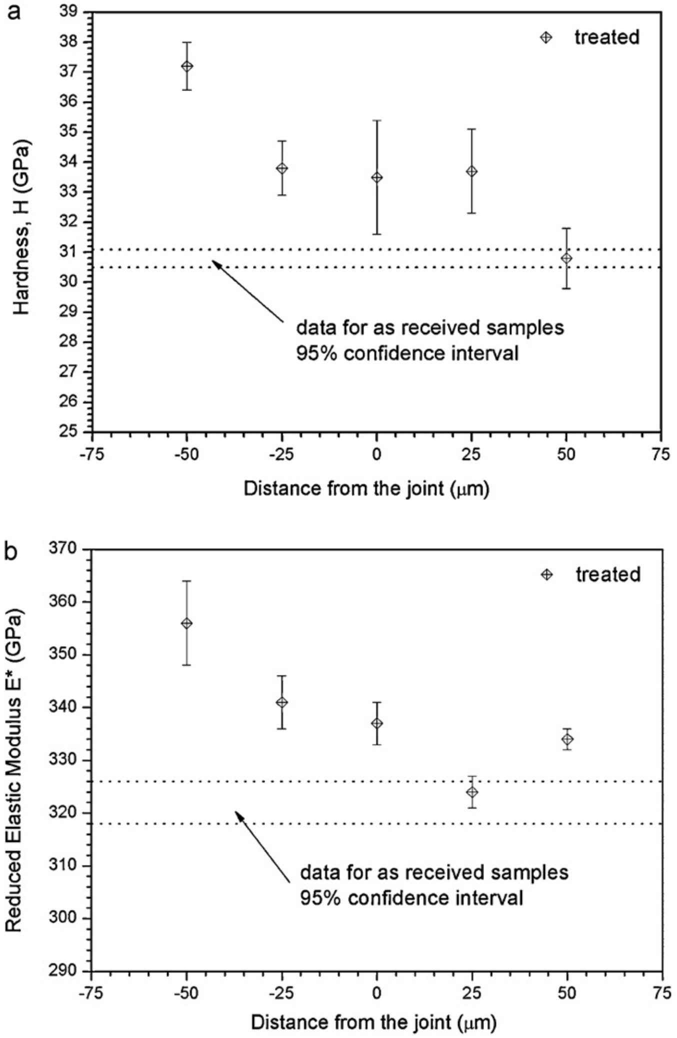

Fig. 6. Plots of hardness (a) and reduced elastic modulus (b), obtained by nano-indentation, versus the distance from the joint.

alumina from the joint might be accommodated in the SiAlON structure. The joining media, in other words, could be dissolved in the parent ceramics.

An evidence of the possibility of dissolution of the joining media into the SiAlON structure comes from the analysis of Fig. 4. Differences in the chemical composition between joint and parent ceramics, at 1550 °C, evidenced by the different grey tones in Fig. 4a, are suppressed by a slight increase of firing temperature at 1570 °C, as shown by Fig. 4b. The integration of the joining media in the structure of the parent ceramics is even more evident by noting, in the same Fig. 4b, the growth of an elongated β-SiAlON crystal across the joint.

Micro- and nano-indentation tests were conducted on samples fired at 1550 °C. The Vickers hardness data as a function of distance from the joints, plotted in Fig. 5a, did not show any significant difference between the joint and the bulk ceramic. This could depend on the above discussed "chemical compatibility" of the joining media to the material to be joined. The trend for indentation fracture toughness confirmed that of Vickers hardness, as illustrated by Fig. 5b (a value of ∼305 GPa for the elastic modulus was selected from previous investigations).[26] The length of cracks emanating from the Vickers indents did not show any increase in the direction of the joint compared to those in the perpendicular direction, suggesting negligible residual stresses in the joint region.

The effect of the indent dimensions (conventional Vickers indents centred in the joint region, due to their width, could test the bulk ceramic on either sides and not solely the joint itself) was excluded by performing nano-indents. Fig. 6a and b shows that the reduced elastic modulus and hardness, measured in a smaller region around the joint than that investigated with micro-indentation, are comparable or slightly higher than that of the SiAlON monoliths to be joined, tested analogously in the as-received condition. Although further mechanical testing will be performed (e.g. indentation tests provide preliminary indirect data, whereas bending strength tests – not possible with the present sample geometry – would provide a direct estimation of the strength of the joints), it may be observed that the mechanical properties are not degraded by the joining.

4. Conclusion

We may conclude that:

- Alumina/silicone nano-composite joints exhibit a chemical and microstructural compatibility with the parent materials;
- The addition of a load during pyrolysis improves the homogeneity of joints;
- The pre-oxidation of SiAlON surface improves only the wetting of the joining media before drying; the flow of silicone resin upon drying allows the formation of an almost continuous and homogeneous coating of SiAlON surfaces even without pre-oxidation;
- Micro- and nano-indentation analyses do not provide any significant evidence of degradation of mechanical properties across the joint.

Future work, besides focusing on the determination of the actual crystal phases in the joint region, will be dedicated to the quantification of the optimum load upon pyrolysis, on the basis of the measurement of the joint strengths.

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