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Short communication

Effect of TiO_2 addition on thermal and mechanical properties of Y–Si–Al–O–N glasses

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Abstract

Y–Si–Al–O–N glasses are intergranular phases in silicon nitride based ceramics in which the composition and volume fraction of oxynitride glass phases determine the sintering/shrinkage behaviour. Several investigations on oxynitride glass formation and properties have shown that addition of nitrogen increases glass transition and softening temperatures, viscosity, elastic modulus and hardness. In the present study, effect of TiO_2 addition on thermal and mechanical properties of Y–Si–Al–O–N glasses is investigated since the most typical Si_3N_4 ceramics for bearing applications are fabricated using a Si_3N_4–Y_2O_3–Al_2O_3–TiO_2–AlN system. Addition of TiO_2 is effective in preparing Y–Si–Al–O–N glasses with lower glass transition temperatures and with higher hardness.

Keywords: C. Hardness; D. Sialon; D. Glass; D. Nitrides; D. Si_3N_4

1. Introduction

Silicon nitride (Si_3N_4) ceramics have excellent mechanical properties which enable them to be used as structural components in severe environments, such as wear parts and engine components.[1–5] During the firing process, oxide additives, such as yttria and alumina, facilitate sintering by reacting with a surface layer of silica on the Si_3N_4 powder particles to form a Y–Si–Al–O–N liquid phase, which allows densification and the transformation of α- to β-Si_3N_4.[1,4–6] On cooling, this liquid phase remains as an intergranular glass either as grain boundary films or at the triple points between grains.[5–7] Y–Si–Al–O–N glasses formed at grain boundaries in Si_3N_4 and SiAlON ceramics are effectively aluminosilicate glasses in which oxygen atoms in the glass network are partially replaced by nitrogen atoms.[7–9] A number of investigations on oxynitride glass formation, structure and properties have sought to understand the nature of these intergranular phases. Properties such as microhardness, Young's and shear moduli, glass transition temperature and viscosity systematically increase with increasing N:O ratio for different series of glasses with fixed cation compositions.[7–9] It has also been shown that the compositions and volume fractions of these glass phases within the silicon nitride or SiAlON ceramics determine their properties, particularly their mechanical behaviour at both ambient and high temperatures.[9]

Si_3N_4 ceramics fabricated from Si_3N_4–Y_2O_3–Al_2O_3–TiO_2–AlN are also now used for bearing applications.[10–12] Several investigations on the sintering behaviour and the microstructural control of ceramics in the Si_3N_4–Y_2O_3–Al_2O_3–TiO_2–AlN system have shown that reactions between TiO_2 and AlN or Si_3N_4 occur to form TiN particles which are dispersed among the β-Si_3N_4/β-SiAlON grains, and this suppresses contact fatigue effects in these silicon nitride-based ceramics.[12,13] It was also shown[14,15] that densification of Si_3N_4 with Y_2O_3/Al_2O_3 additives is promoted at lower temperatures by the simultaneous addition of TiO_2 and AlN to the Si_3N_4–Y_2O_3–Al_2O_3 system, which is very important for lower cost mass production of Si_3N_4-based ceramics. These results indicate that Ti atoms dissolve in the Y–Si–Al–O–N liquid phase and should have some effect on the glass properties; however, no previous investigations on the properties of Ti–Y–Si–Al–O–N glasses have been reported.

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Table 1
Composition of the samples.

Sample	Y	Al	Ti	Si	O	N
Ti0 N0	28	16	0	56	100	0
Ti0 N10	28	16	0	56	90	10
Ti0 N20	28	16	0	56	80	20
Ti0.5 N0	27.86	15.92	0.5	55.72	100	0
Ti0.5 N10	27.86	15.92	0.5	55.72	90	10
Ti0.5 N20	27.86	15.92	0.5	55.72	80	20
Ti1.0 N0	27.72	15.84	1	55.44	100	0
Ti1.0 N10	27.72	15.84	1	55.44	90	10
Ti1.0 N20	27.72	15.84	1	55.44	80	20

In the present study, therefore, small additions of TiO_2 were added to Y–Si–Al–O–N glasses of similar cation compositions to those present in the grain boundaries of silicon nitride ceramics in order to study the effect of Ti on properties such as glass transition temperature and microhardness.

2. Experimental procedure

The compositions of oxynitride glasses are expressed in equivalent percent (eq.% or e/o) of cations and anions instead of atoms or gram-atoms.[7–9] One equivalent of any element always reacts with one equivalent of any other element or species. For a system containing four types of cations, A, B, C and D with valencies of v_A, v_B, v_C and v_D, respectively, then:

$$A\,(\text{eq.\%}) = 100\cdot(v_A[A])/(v_A[A] + v_B[B] + v_C[C] + v_D[D]) \tag{1}$$

where [A], [B], [C] and [D] are, respectively, the atomic concentrations of A, B, C and D, in this case, Si^{IV}, Al^{III}, Y^{III} and Ti^{IV}.

If the system contains two types of anions, E and F with valencies v_E and v_F, respectively, then:

$$E\,(\text{eq.\%}) = 100\cdot(v_E[E])/(v_E[E] + v_F[F]), \tag{2}$$

where [E] and [F] are, respectively, the atomic concentrations of E and F, in this case O^{II} and N^{III}.

In the present study, a basic yttrium aluminosilicate glass was prepared with a cation composition (in eq.%) of 28Y:56Si:16Al and two further glasses were prepared with substitution of 10 eq.% and 20 eq.% N for oxygen. Six further glasses were prepared with addition of 0.5 eq.% or 1 eq.% Ti but keeping the Y:Si:Al and O:N ratios constant as shown in Table 1. These glasses were prepared using high purity (99.9%) TiO_2 (Aeroxide P25, Nippon Aerosil Co. Ltd.), Y_2O_3 (RU, Shinetsu Chemical Co.), SiO_2 (Fluka Chemika), Al_2O_3 (Sumitomo Chemical Co.), and Si_3N_4 (Ube Co. Ltd.) powders. The surface silica on the Si_3N_4 powder was noted, in calculating the glass compositions, as being 1.28 wt% oxygen, equivalent to 2.47 wt% silica. For the preparation of glass samples, a batch of 20 g was prepared and milled in a ball mill under dry conditions with alumina as milling media for 5 h. 20 g samples were pressed uniaxially under a pressure of 50 MPa to form compacts.

The powder compacts were melted in BN (Boron nitride) lined graphite crucibles in a lanthanum chromite vertical tube furnace at 1700 °C under 0.1 MPa flowing nitrogen for 1 h after which the crucible was rapidly withdrawn from the furnace and the glass melt poured into a pre-heated graphite mould and annealed for 1 h at T_g prior to slow furnace cooling to ambient temperature in a muffle furnace. The use of BN coated graphite crucibles helped to maintain slightly reducing conditions as well as facilitating the pouring of the glass melt from the crucible after firing.

The samples were analysed by conventional X-ray diffraction (RINT2500, Rigaku, Japan) using CuKα radiation operated at 50 kV and 300 mA in order to detect any crystalline phases in the samples. Densities were measured by the Archimedes principle, using distilled water. Microhardness tests were carried out on polished glass samples using a Leco microhardness tester. Indentation diagonals were measured to give an estimation of the hardness of the glass. Differential thermal analysis was carried out in order to determine the glass transition and crystallization temperatures. Samples were placed in BN-lined alumina crucibles in a flowing nitrogen atmosphere at a rate of 5 °C/min up to 1300 °C. Al_2O_3 was used as the reference material. Glass transition temperature was also confirmed by a dilatometric measurement using a Netzsch dilatometer (model 402 C, Selb) and alumina as the reference material for calibration of the instrument. Polished samples of $10 \times 3 \times 3\ \text{mm}^3$ were heated at a rate of 5 °C/min under flowing nitrogen gas and the corresponding length increase was recorded by a displacement gauge accurate to 1.25 nm. The curve obtained was modified by subtracting the expansion of the alumina push rod from it.

3. Results and discussion

It was confirmed that no crystalline phases were formed in any of the nine glass samples shown in Table 1, indicating that Ti atoms are dissolved in these glasses. However, it should be noted that formation of crystalline TiN was observed when 2.0 eq.% of Ti was added to these Y–Si–Al–O–N glasses. This is supported by the fact that TiN particles are formed by the reaction between TiO_2 and AlN or Si_3N_4 among Si_3N_4 grains in the Si_3N_4–Y_2O_3–Al_2O_3–TiO_2–AlN system. Density of oxynitride glasses as a function of concentration of Ti and N are shown in Fig. 1. For the oxynitride glasses, density increases linearly with the addition of nitrogen. The higher density of glasses means that there is a significant reduction in volume due to the incorporation of tri-coordinated nitrogen and this is confirmed by the significant increase in density. This improvement in physical properties of oxynitride glasses with increase in nitrogen is consistent with the previous reports on oxynitride glasses.[7–9,16,17] It can be seen that the addition of Ti to both oxide and oxynitride glasses does not systematically change their densities. It was expected that disruption of the glass network by the inclusion of 0.5 or 1 eq.% Ti would decrease the density of oxide and oxynitride glasses but the fact that it did not change can be attributed to simultaneous changes in the volume by the addition of Ti atoms.

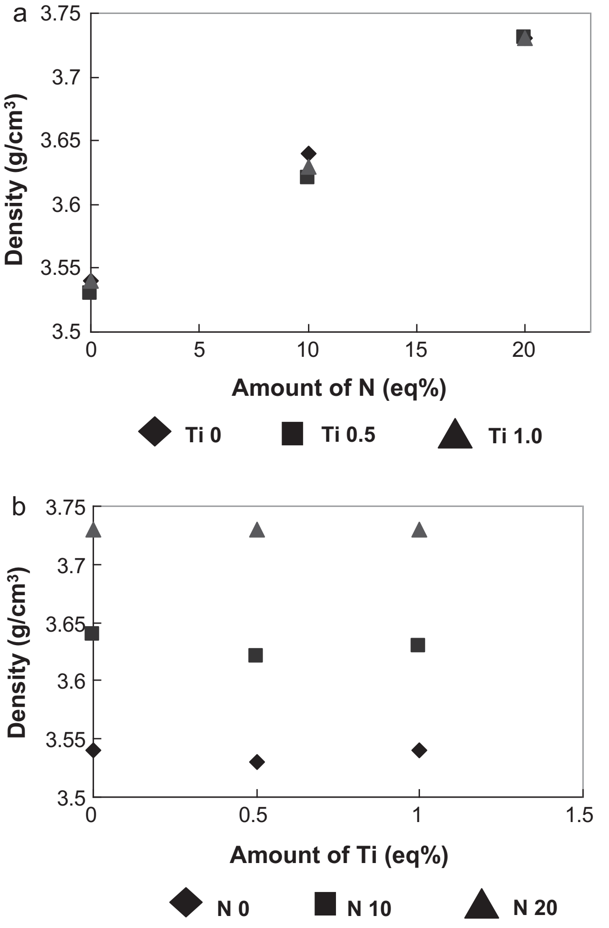

Fig. 1. Density of the Ti–Y–Si–Al–O–N glasses. Density as a function of (a) amount of nitrogen and (b) amount of titanium.

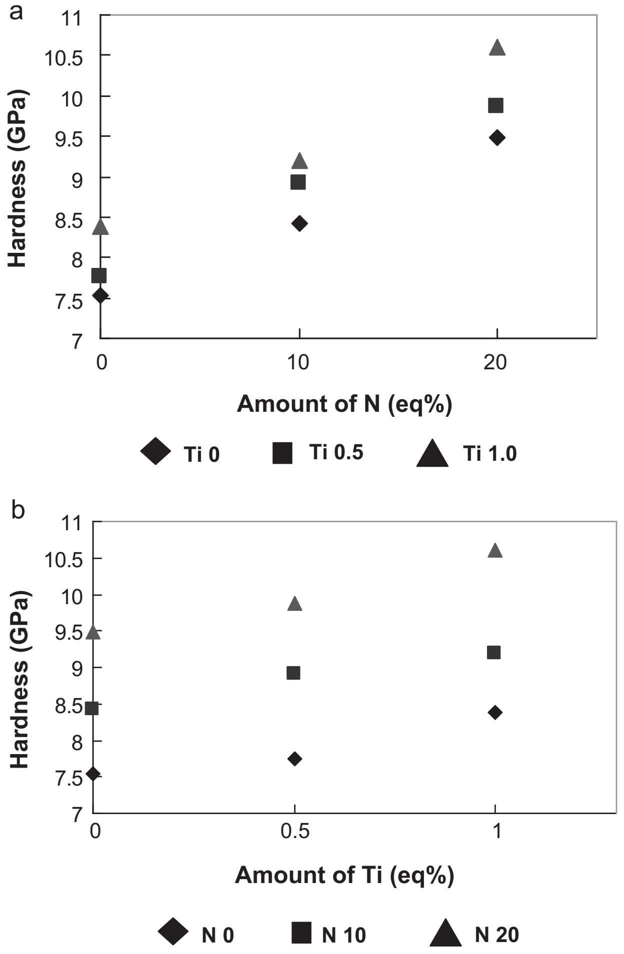

Fig. 2. Hardness of the Ti–Y–Si–Al–O–N glasses. Hardness as a function of (a) amount of nitrogen and (b) amount of titanium.

Fig. 2 shows the microhardness of the samples. The effect of nitrogen on the mechanical properties is obvious as it results in an increase in the values of microhardness. Evaluating the microhardness of the samples reveals that, for the same Ti concentration, higher hardness values are obtained with the addition of 20 eq.% N, indicating that with replacement of divalent oxygen by tri-coordinated nitrogen, more rigid glasses are obtained. Improvement of the mechanical properties with nitrogen addition was also confirmed in earlier studies of oxynitride glasses.[7–9,16,17] Addition of Ti also has a positive effect on microhardness of oxide and oxynitride glasses. Since formation of TiN, a typical hard material, was not confirmed in any of the glass samples, the increase in microhardness may be attributable to the solid solution effect of Ti within the glass structure and it appears that its disruptive effect as a network modifier on glass network structure is insignificant.

Young's moduli of the glasses are shown in Fig. 3. In general, the Young's modulus is a function of the atomic network compactness and the bond energy.[18] These two parameters determine the variation of the Young's modulus when a change in glass chemical composition occurs. The value of bond energy for Si–N bonds, $U_{0\,\mathrm{Si–N}}$ (437 kJ/mol), is smaller than for Si–O bonds, $U_{0\,\mathrm{Si–O}}$ (800 kJ/mol), so the reason for glass being stiffer with nitrogen is more related to the higher glass compactness which is a result of the increase in density. Therefore it can be deduced that the more compact glasses show higher values of Young's modulus as shown in Fig. 3a. Also it was observed that the addition of Ti does not influence the density of oxide or oxynitride glasses significantly as shown in Fig. 1 and hence similar values for Young's modulus are confirmed for each series as shown in Fig. 3b.

Glass transition temperature of oxide and oxynitride glasses as a function of the amount of N and Ti concentration are given in Fig. 4. Nitrogen addition improves the cross-link density of the network by the formation of $N{\equiv}(SiO_3)_3$ and $-N{=}(SiO_3)_2$ linkages. This increases the thermal energy needed for the mobility of the structural units as they are more strongly bonded together.[7–9,16–18] As can be seen in Fig. 4, nitrogen substitution for oxygen increases the glass transition temperature. Higher values of T_g for the oxynitride glasses compared with oxide glasses, at constant Ti content, reveal the constructive role of nitrogen within the glass structure.

For example, in Ti free samples, the recorded slope of T_g versus N content was

$$T_g = 902 + 3(\mathrm{N\,eq.\%}) \qquad (3)$$

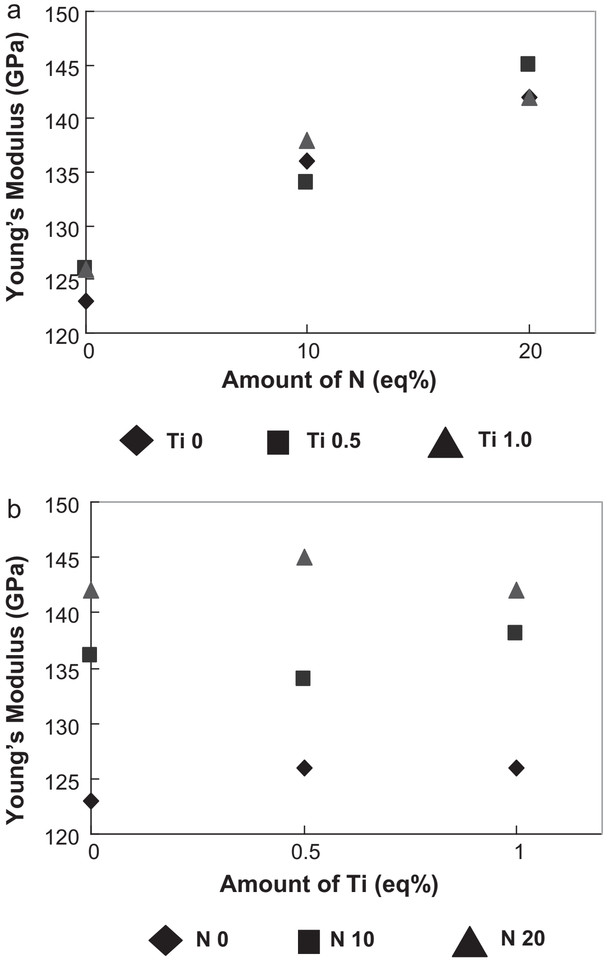

Fig. 3. Young's modulus of the Ti–Y–Si–Al–O–N glasses. Young's modulus as a function of (a) amount of nitrogen and (b) amount of titanium.

(N 0: 902 °C → N 10: 939 °C → N 20: 962 °C). When nitrogen is incorporated into the glass, more energy is required in order to reach the viscosity corresponding to T_g compared with a nitrogen free glass. It is clear that addition of Ti lowers the glass transition temperatures consistently and linearly in oxynitride samples while, in nitrogen free samples, T_g is almost constant. When Ti is added to these glass compositions, the amounts of the other cations, Y (modifier) and the network forming ions, Si and Al are all decreased slightly. Ti is known to be an intermediate ion between network formers and modifiers in silicate glasses but it has a lower cation field strength than Al. Ti has been reported[19,20] to exist in different coordination states with oxygen, the most prevalent being as TiO_5 tetragonal pyramids containing one non-bridging oxygen atom associated with a titanyl bond. As Ti increases, then more non-bridging ions are likely to be formed and the glass network is disrupted. When nitrogen is present in the glasses, then Ti may bond with nitrogen, which affects the modifying effect on the glass network and the network connectivity is more disrupted with a consequent lowering of T_g of the glasses.

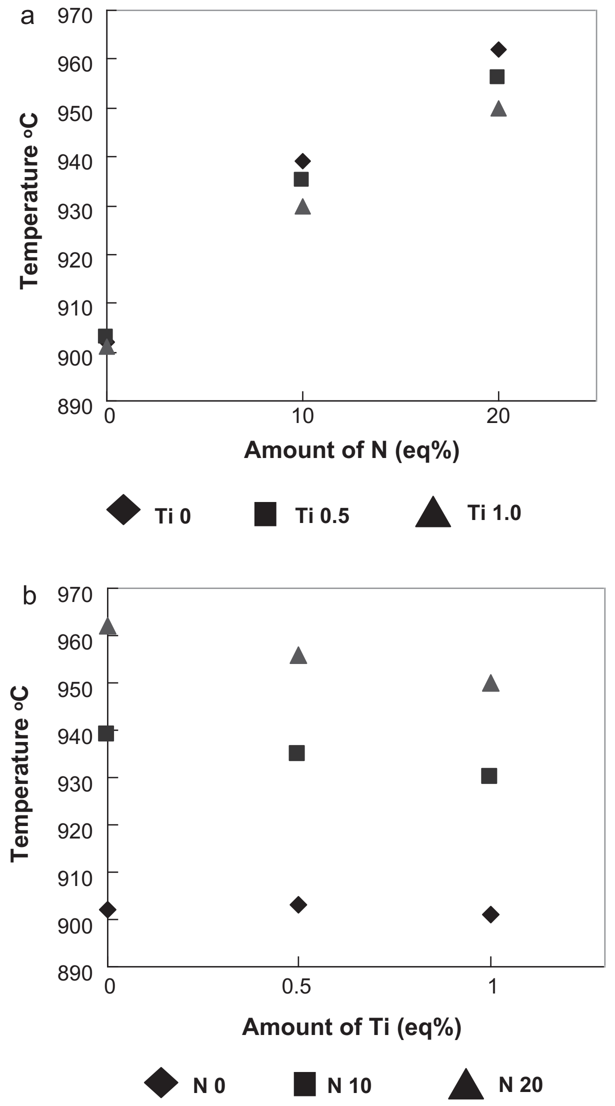

Fig. 4. Glass transition temperature (T_g) of the Ti–Y–Si–Al–O–N glasses. T_g as a function of (a) amount of nitrogen and (b) amount of titanium.

Whilst TiN could not be detected by XRD or any microscopic methods, nevertheless, very tiny crystals of TiN might be formed by reaction of Ti with N in the glass. Regarding N 20 samples, T_g decreases with increasing Ti content (Ti 0: 962 °C → Ti 0.5: 956 °C → Ti 1.0: 950 °C). If all Ti atoms react with N to form TiN in the "Ti 1.0, N 20" sample, the glass composition would be changed as follows:

$$\begin{array}{cccccc} Y & : Si & : Al & : Ti : & O : & N \\ 27.44 & 54.88 & 15.68 & 2.0 & 80 & 20 \end{array} \Rightarrow \begin{array}{ccccc} Y & : Si & : Al & : O & : N \\ 28 & 56 & 16 & 81.22 & 18.78 \end{array} + \mathrm{TiN} \qquad (4)$$

The remaining Y–Si–Al–O–N glass would contain a smaller amount of N (18.8 eq.%) in the glass network which would result in a lower glass transition temperature. Based on this assumption and taking into account Eq. (4), the estimated decrease of T_g is 1.8 °C. This value is much lower than the actual observed decrease of T_g (12 °C; Ti 0: 962 °C → Ti 0.5: 956 °C → Ti 1.0: 950 °C), indicating that Ti atoms do not react with N to form crystalline TiN but Ti atoms form weak titanyl bonds to non-bridging ions[20] resulting in a much greater reduction in T_g for these oxynitride glasses with Ti. These results are consistent with the fact that addition of TiO_2 to silicon nitride ceramics in the Si_3N_4–Y_2O_3–Al_2O_3 system promotes densification at lower sintering temperatures[14,15] although further investigations are needed, for example, X-ray absorption and spectroscopic measurements, to elucidate the details of the intergranular Ti–Y–Si–Al–O–N glass phases in these types of silicon nitride ceramics.

4. Conclusions

The effect of TiO_2 additions on thermal and mechanical properties of Y–Si–Al–O–N glasses was investigated in order to understand the properties of intergranular phases in silicon nitride ceramics in the Si_3N_4–Y_2O_3–Al_2O_3–TiO_2–AlN system for bearing applications. It was found that the addition of Ti to both oxide and oxynitride glasses does not systematically change their densities and Young's moduli but results in higher hardness. On the other hand, addition of TiO_2 is effective in lowering glass transition temperatures of Y–Si–Al–O–N glasses consistently and linearly, which supports the fact that densification is promoted at lower temperatures in the sintering process of Si_3N_4 silicon nitride ceramics in the Si_3N_4–Y_2O_3–Al_2O_3 system by the simultaneous addition of TiO_2 and AlN.

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