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Si_3N_4–AlN Polytypoid Composites by GPS

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Abstract

Through the tailoring of phase compositions of materials, dense Si_3N_4–AlN polytypoid composites were fabricated by gas pressure sintering (GPS) from the mixtures of the powders of Si_3N_4, AlN and Al_2O_3, using La_2O_3 as additive. The phase compositions of the ceramics obtained are composed of β-sialon and 12H polytypoid as two major crystalline phases and a liquid within the La–Al–Si–O–N system as grain boundary phase. The effect of the content of AlN polytypoid in the matrix and the amount of La_2O_3 doping as additive on the densification, microstructure and mechanical properties were described.

Durch speziell ausgewählte Phasenzusammensetzungen konnten durch Gasdrucksintern (GPS) dichte Si_3N_4-Verbundwerkstoffe mit einem AlN-Polytyp als verstärkender Phase hergestellt werden. Als Ausgangsmaterial wurden Pulvermischungen aus Si_3N_4-, AlN- und Al_2O_3-Pulver unter Zugabe von La_2O_3 verwendet. Das Gefüge dieser Keramiken setzt sich hauptsächlich aus zwei kristallinen Phasen, β-Sialon und dem 12H Polytyp, und einer glasigen La–Al–Si–O–N Korngrenzenphase zusammen. Auf den Einfluß des AlN-Polytyp-Anteils in der Matrix und der als Sinteradditiv zugegebenen La_2O_3-Menge auf die Verdichtung, das Gefüge und die mechanischen Eigenschaften wird eingegangen.

On a élaboré des composites denses de polytypes de Si_3N_4–AlN par frittage sous pression de gaz (GPS) à partir de mélanges des poudres Si_3N_4, AlN et Al_2O_3 en utilisant La_2O_3 comme additif et en adaptant la composition des phases des matériaux. Les compositions obtenues sont constituées des phases cristallines majoritaires β-sialon et du polytype 12H ainsi que d'une phase liquide du système La–Al–Si–O–N située aux joints de grains. On décrit ici les effets de la teneur en polytype AlN dans la matrice et de la quantité d'additif La_2O_3 sur la densification, la microstructure et les propriétés mécaniques du matériau.

1 Introduction

In recent years, multiphase ceramics have become more and more interesting[1] in their advantage of summing-up to some extent the favorable properties of single phases, which can be obtained by tailoring the phase compositions and the microstructures of materials combining with advanced processing.

In the nitrogen-rich area of the Si–Al–O–N system (Fig. 1), there exist many sialon polytypoids—8H, 15R, 12H, 21R, 27R and $2H^{\delta}$, which are each in equilibrium with β-Si_3N_4.[2] These phase relationships provide the possibility of tailoring and synthesizing a two-phase ceramic of β-Si_3N_4–AlN

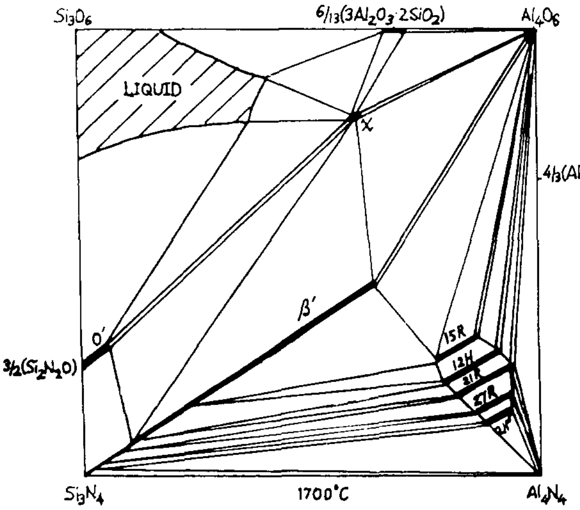

Fig. 1. Si–Al–O–N system.[2]

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polytypoid. However, the compositions located on the nitrogen-rich area in the Si–Al–O–N system are usually more difficult to fabricate than those on the oxygen-rich side of β-sialon, which are usually chosen to synthesize β-sialon single-phase ceramics. Therefore, gas pressure sintering (GPS) under higher N_2 pressure and doping La_2O_3 as additive were used in the present work to promote densification. It is expected that the material will be strengthened by the reinforcement of the columnar AlN polytypoid phase formed *in situ*, together with the intimate combination of the two major phases with each other.

The present work gives a preliminary report on the tailoring of phase compositions and synthesizing of the two-phase ceramics by GPS, along with their mechanical property studies.

2 Experimental

The starting powders used were Si_3N_4 (Starck LC12, grain size 1 μm) AlN (6 μm), Al_2O_3 (1 μm) and La_2O_3 (1 μm) (Chinese made, oxides are 99·9% purity). The compositions designed for the investigation are shown in Tables 1 and 2, in which the nominal ratio of AlN:Al_2O_3 used from starting powders corresponds to the composition of 21R polytypoid. The mixtures of the powders were milled, formed and embedded in the packing powder of 90 wt% Si_3N_4 + 10 wt% BN, and then fired by GPS at 1900°C under 1 MPa N_2 for 3 h. GPS has proved to be an effective processing method for protecting nitrides from decomposition and promoting densification.[3,4]

The phase compositions of samples were analyzed by X-ray diffraction and EDAX. The flexure strength was measured by the three-point method and the fracture toughness, K_{Ic}, was determined by the SENB method.

Table 1. Compositions with 2 wt% La_2O_3 additive

Samples	*Compositions* (*wt%*)	
	Si_3N_4	*21R AlN polytypoid*
SAL-1	89	9
SAL-2	83	15
SAL-3	78	20
SAL-4	73	25
SAL-5	65	33

Table 2. Compositions with 25 wt% AlN polytypoid

Samples	*Compositions* (*wt%*)	
	Si_3N_4	*La_2O_3*
SAL-6	75	0
SAL-7	74·5	0·5
SAL-8	74	1
SAL-4	73	2
SAL-9	70	5
SAL-10	68	7

3 Results and Discussion

3.1 Phase compositions

For tailoring the content of AlN polytypoid in the matrix of two-phase ceramics, five compositions, all with 2 wt% La_2O_3 as additive, listed in Table 1, were processed by GPS. The sample SAL-4 with the nominal composition of 25 wt% polytypoid has the highest density and bending strength of all five compositions, as shown in Fig. 2. Therefore, SAL-4 was chosen for the follow-up experiments as the reference material. The phase compositions of the sample SAL-4 after GPS are composed of β-sialon and 12H AlN polytypoid with a trace of 15R or 21R and the liquid as grain boundary phase. The ratio of β-sialon to 12H was semi-quantitatively estimated to be 80:20 by X-ray diffraction, as shown in Fig. 3. It shows a deviation of about 5% from the nominal composition of 75:25.

In the phase diagram of the AlN–Al_2O_3 binary system reported by McCauley & Corbin,[5] 12H could be formed only at temperatures higher than 2050°C. In the present work, however, the reaction of AlN–Al_2O_3 and Si_3N_4 could occur and form 12H at 1900°C under higher N_2 pressure. The composition of 12H sialon polytypoid in sample SAL-4 was analyzed by EDAX to have ratios Al:Si = 74·3:25·7 = 4·46:1·54 (for a total of 6 metal atoms), i.e. $Al_{4 \cdot 46}Si_{1 \cdot 54}O_{1 \cdot 46}N_{5 \cdot 54}$ or 3·48AlN:0·49Al_2O_3:

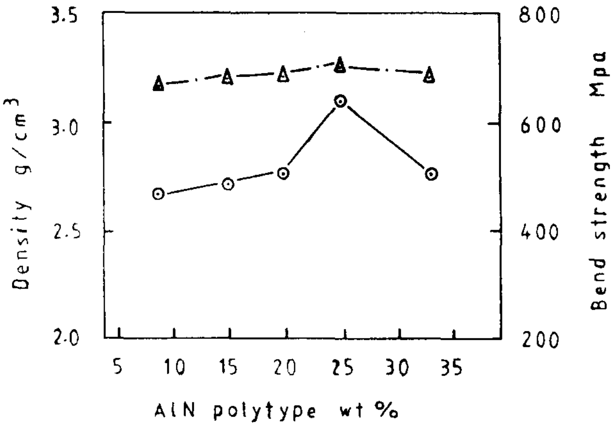


Fig. 2. Density and bending strength versus AlN polytypoid (wt%).

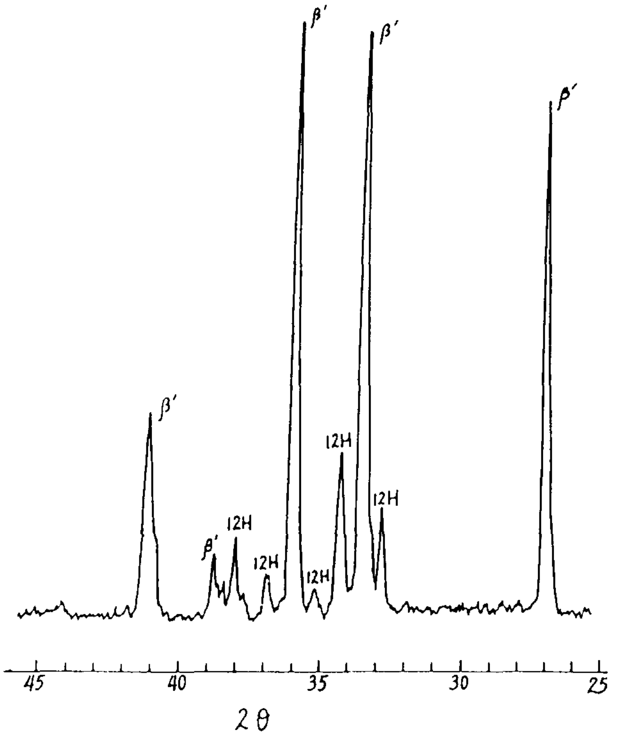
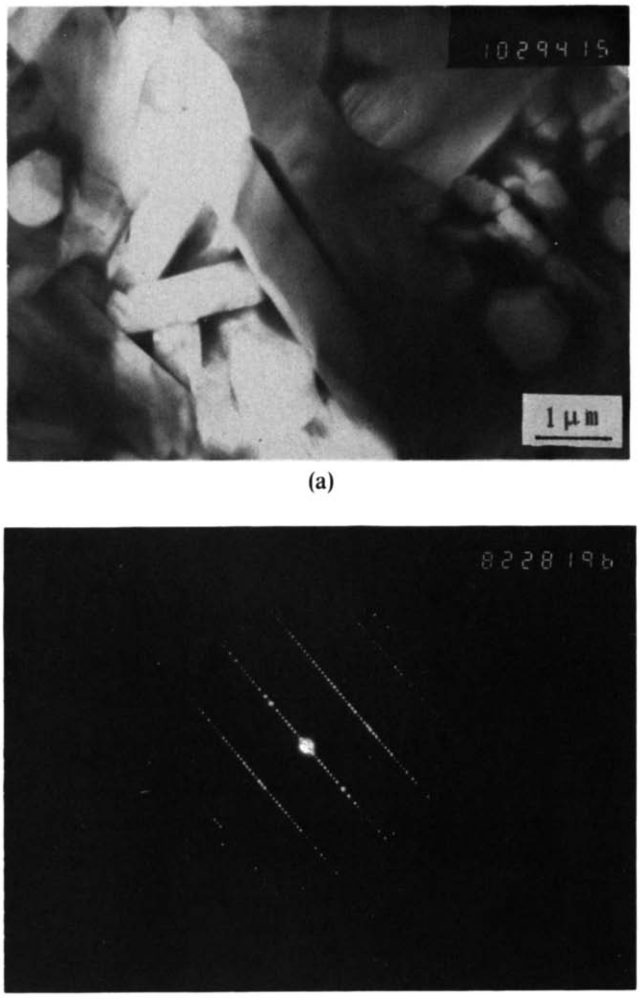


Fig. 3. X-ray diffraction pattern of SAL-4 sample.



(a)

(b)

Fig. 4. (a) Transmission electron micrograph of SAL-4 sample; (b) electron diffraction pattern of 12H polytypoid.

$0{\cdot}514Si_3N_4$. It seems that the reaction of AlN–Al_2O_3 (according to the compositional ratio of 21R) and Si_3N_4 produced three results: most of AlN–Al_2O_3 was used to form 12H with a trace of 15R or 21R, a part participated in the formation of β-sialon as the main phase and the rest reacted with La_2O_3 and SiO_2 (on the surface of Si_3N_4 particles) forming the glassy phase of the La–Al–Si–O–N system as the grain boundary phase.

The compositions of the glassy phase at the grain boundaries were analyzed by EDAX to have ratios of about La:Al:Si = 33:35:32 at.%. The TEM micrograph of the sample (Fig. 4(a)) shows the columnar crystals of polytypoid and its electron diffraction pattern (Fig. 4(b)) gives the hexagonal structure of 12H.

3.2 Role of La_2O_3

For choosing the optimum amount of La_2O_3 doped as additive, six compositions, all with 25 wt% polytypoid (listed in Table 2), were prepared. Figure 5 shows the density variation of the six samples after GPS with different amounts of La_2O_3 doping. The sample SAL-6, without La_2O_3, gave a density of only 2·16 g/cm^3 (about 68% theoretical density), indicating that nearly no densification had occurred. With only 0·5 wt% La_2O_3 doping, the density abruptly increased up to 94% TD. By further increasing the dopage of La_2O_3 from 1–7 wt%, a densification of over 98% TD could be obtained. It is evident that La_2O_3 facilitates the formation of a liquid phase which promotes the densification of the samples and the formation of β-sialon and 12H polytypoid through the reaction and the 'solution–precipitation' process of Si_3N_4, AlN and Al_2O_3 with the help of the liquid phase. The effect of La_2O_3 additive amount on the β:12H ratio is not obvious. The content of 12H varies from 15–20% when doped with 0–7 wt% of La_2O_3 as investigated

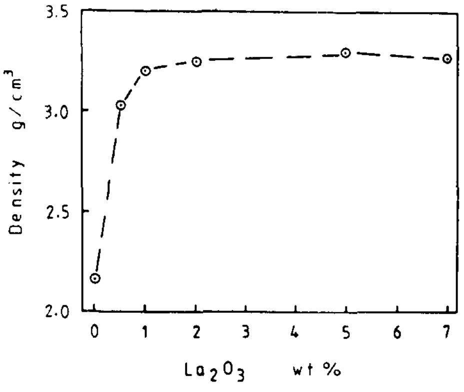


Fig. 5. Density versus La_2O_3 (wt%).

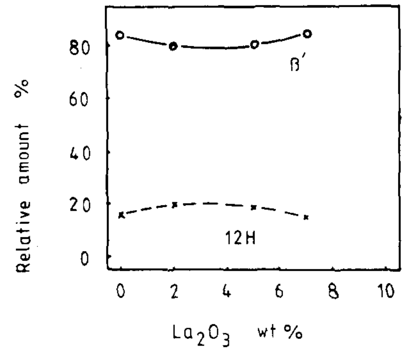


Fig. 6. Relative phase amount versus La_2O_3 (wt%).

(Fig. 6). However, too much La_2O_3 doping will produce excessive glassy phase, having adverse effects on material properties. Thus, further experiments have been carried out to study the effect of La_2O_3 amount on the properties of materials.

3.3 Properties and microstructures

The effect on the strength and the fracture toughness of the samples with different amounts of La_2O_3 is shown in Figs 7 and 8. It seems that the amount of La_2O_3 additive from 2–5 wt% does not make a big difference on their properties, although the samples doped with 5 wt% La_2O_3 have the highest bending strength of 739 MPa. The mechanical properties could be related to the corresponding microstructure of the samples. Figure 9 shows electron micrographs of the microstructures of samples doped with 1, 2 and 5 wt% La_2O_3 respectively. It is obvious that the sample with 5 wt% La_2O_3 has a

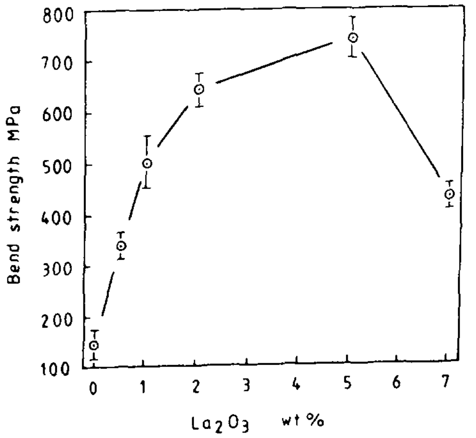


Fig. 7. Bending strength versus La_2O_3 (wt%).

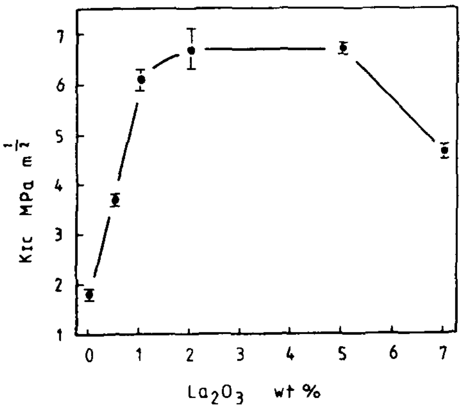
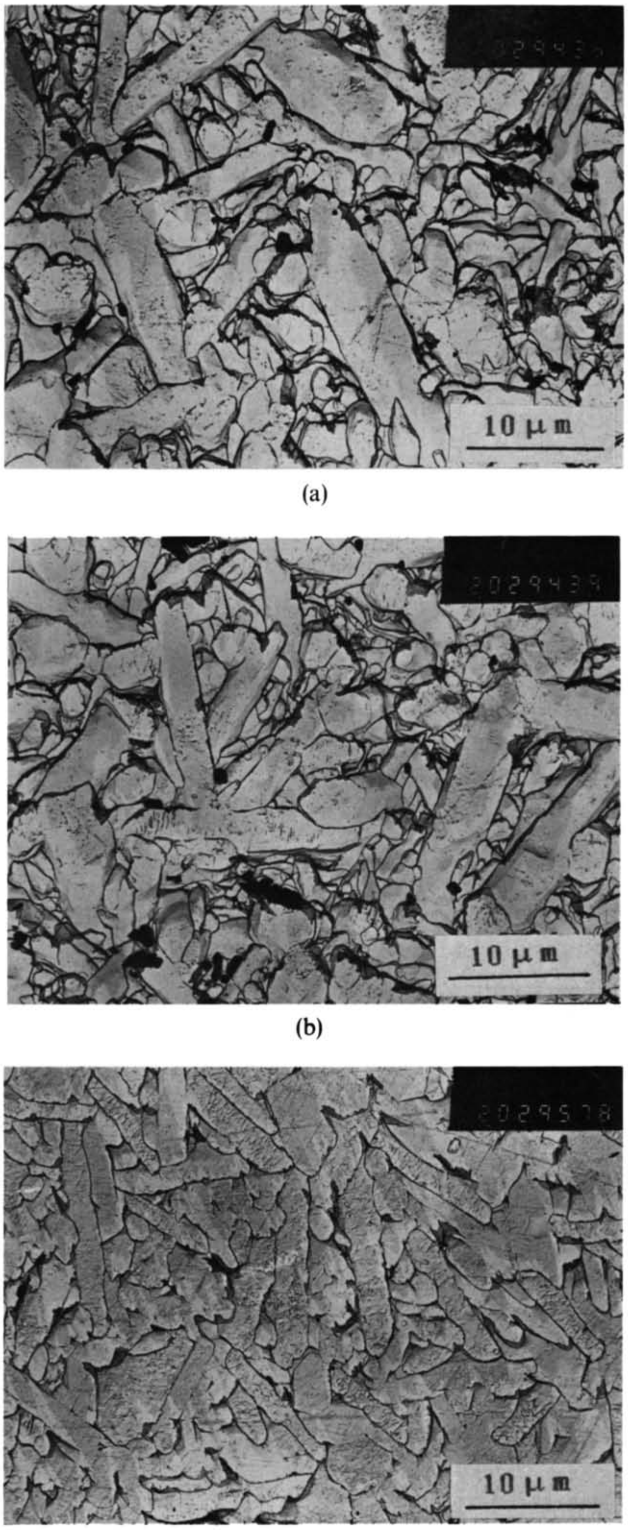


Fig. 8. Fracture toughness K_{Ic} versus La_2O_3 (wt%).



(a)

(b)

(c)

Fig. 9. Electron micrographs of samples. (a) 1 wt% La_2O_3; (b) 2 wt% La_2O_3; (c) 5 wt% La_2O_3.

much finer and homogeneous microstructure with embedded elongated grains. This optimum microstructure with the columnar crystals formed *in situ* as one of the main phases supports the fact of its having high mechanical properties.

4 Conclusions

(1) On the basis of compositional tailoring, the Si_3N_4–AlN polytypoid composites were fabricated by GPS from the mixture of powders of Si_3N_4, AlN and Al_2O_3 using La_2O_3 as additive.

(2) The phase composition of this composite is composed of β-sialon and 12H polytypoid with a ratio of β:12H = 80:20 as the two major phases and the glassy grain boundary phase.

(3) The effect of the amount of La_2O_3 doping on the densification, mechanical properties and the microstructures was discussed.

(4) The samples doped with 5 wt% La_2O_3 as additive has the highest bending strength of 739 MPa and the fracture toughness K_{Ic} of 6·7 MPa $m^{1/2}$. The finer microstructure with columnar crystals formed *in situ* is favorable for materials to have good mechanical strength and fracture toughness.

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