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Effect of amount and atomic ratio of dual modifiers Ca and Mg on phase formation and mechanical properties of Ca,Mg-α-Sialons

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Multi-cation α-Sialons ceramics containing calcium and magnesium for the compositions ((Ca,Mg)$_x$Si$_{12-3x}$Al$_{3x}$O$_x$N$_{16-x,}$), where x equals 0.6 and 1.0 with the different atomic ratios of Ca to Mg, were fabricated by hot-pressing. An exploration for Ca,Mg-α-Sialon involving phase compositions, cell dimensions, microstructure and mechanical properties were carried out in the present work. © *2000 Kluwer Academic Publishers*

1. Introduction

During the sintering of α-Sialon [1] (abbreviated as α'), whose general formula is represented as $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ (M = Li, Ca, Mg, Y and part of rare earth elements, $x = m/v$, v to be the valency of the cation), oxide additives are usually used to promote densification by forming a liquid phase with the oxide on the surface of nitride starting powder. Consequently, the transient liquid phase can be absorbed into Si_3N_4 by forming α'. Therefore, the formation of α' is expected to provide the advantage of incorporating cations as a sintering additive into the Si_3N_4 structure, thus cleaning the grain boundary region and improving the high temperature strength. In recent years, some investigations dealing with dual cation α' materials have been reported [2–4] as it was thought the dual modifiers materials, for example, resulted in a lower eutectic temperature. In our previous work, dual cations, with equal atomic ratio of Ca and Mg, were used to form α' ceramics. The results have shown that the materials possessed an improved sintering ability, as the bulk densities of Ca,Mg-α' were obviously higher than its counterpart single cation Ca-α' [5]. It was also found that most of the added Ca^{2+} and much less of Mg^{2+} have been incorporated into the α' structure, whereas most of the added Mg^{2+} entered sialon polytypoid phase. Mg^{2+} can be absorbed into AlN-polytypoid structure to form magnesium containing AlN-polytypoid phase was reported by Thompson etc [6]. The formation of magnesium containing AlN-polytypoid phase in Ca,Mg-α' is thus considered to provide a possibility to reduce the amount of glassy phase at the grain boundary, like α'. In fact, in comparison with Ca-α', both the hardness and fracture toughness of Ca,Mg-α' for the same composition were higher and the improved hardness of Ca,Mg-α' materials were attributed to the reduced glassy phase at the grain boundary in a series of (Ca,Mg)-α's, besides the better sintering ability of Ca,Mg-α's [5]. A further study of multi-cation Ca,Mg-α-sialons with various atomic ratios of Ca to Mg is therefore worthy to be continued. The effects of the amount of additives and atomic ratios of Ca to Mg on the phase compositions, cell dimensions, microstructures and mechanical properties of Ca,Mg-α' were investigated in the present work.

2. Experimental

The nominal compositions used were $M_xSi_{12-3x}Al_{3x}O_xN_{16-x}$, i.e. $x = m/2 = n$ with the values of 0.6 and 1.0. The atomic ratios of Ca to Mg in the compositions were 0.2 : 0.4, 0.4 : 0.2 for $x = 0.6$ and 0.3 : 0.7, 0.7 : 0.3 for $x = 1.0$ respectively (named as BCM24, BCM42, CCM37 and CCM73). The starting powder used were Si_3N_4 (UBE-10, Japan, 2.0wt%O), AlN (1.3wt%O), $CaCO_3$ (99.0%) and MgO (99.0%). The mixtures were milled in an agate mortar under absolute alcohol for 1.5 h. Powders were dried and then hot-pressed (20 MPa) at 1750°C for 1 h in a graphite-resistant furnace under a flowing nitrogen of 1 atmosphere. Before reaching the holding temperature, the powder mixture was firstly kept at 1150°C for 0.5 h to complete the decomposition of $CaCO_3$. The bulk densities of the samples were measured by the Archimedes principle. Phase assemblages were characterized by X-ray diffraction using a Guinier-Hägg camera with Cu $K_{\alpha1}$ radiation and Si as an internal standard. The measurement of X-ray film and refinement of lattice parameters were completed by a computer-linked line scanner (LS-18) system [7] and SCANPI, PIRUM [8] programs. The microstructure observation was performed under a SEM (KYKY 2000, China) on the surfaces of samples etched by melting NaOH, which were polished before etching. The surface of fractured sample, which was obtained after testing the flexural strength, was also observed by SEM. Hardness and indentation fracture toughness was measured by using a Vickers diamond indenter under a load of 100 N. Flexural strength was tested by three-point bending with a 30 mm span.

3. Results and dicussion

3.1. Densification and phase formation

The measured bulk densities D_m and the phase assemblages of the compositions with various atomic ratios of Ca to Mg are summarized in Table I. The calculated densities D_{cal} and the ratios of D_m to D_{cal} are also given in the Table. It should be pointed out that it was difficult to estimate the accurate calculated densities because of existence of other phases in the samples besides α'. The phase assemblages of materials were therefore considered to be composed of only one phase α' to estimate the calculate densities and the data of D_{cal} were obtained based on formulas and lattice parameters of Ca,Mg-α' determined in the present work (see Table II). It can be understood that the calculated densities would be higher than the corresponding measured values, especially for CCM73 and CCM37, which contain a small amount of Mg AlN-polytypoid phase in the materials. For measured densities of the samples, as seen from Table I, the bulk densities of BCM24 and BCM42 were similar, although the weight of nominal formula of BCM24 was smaller than that of BCM42. The similar density indicated that BCM24 possessed the better sintering ability than that of BCM42, which was attributed to the liquid-rich composition caused by higher amount of MgO in BCM24 than in BCM42. For $x = 1.0$ compositions, the values of measured bulk densities of CCM37 and CCM73 were little different. The more the amount of Mg in the composition was, the better the sintering ability of sample. This trend of bulk density was the same as $x = 0.6$ case.

TABLE I Density and phase present of Ca,Mg-α' samples hot-pressed at 1750°C

Sample	x value	Ca : Mg (at%)	Bulk density D_{cal} (g/cm^3)	D_m (g/cm^3)	D_m/D_{cal}	Phase present
BCM24	0.6	0.2 : 0.4	3.217	3.20	99.5	α'/s, α/tr, AlN$'^a$/tr
BCM42	0.6	0.4 : 0.2	3.223	3.20	99.3	α'/s, α/vw
CCM37	1.0	0.3 : 0.7	3.259	3.23	99.1	α'/s, AlN$'$/mw
CCM73	1.0	0.7 : 0.3	3.277	3.21	98.0	α'/s, AlN$'$/w

[a] AlN$'$ = Mg AlN-polytypoid, s = strong, m = medium, w = weak, vw = very weak, tr = trace.

TABLE II Lattice parameters of Ca,Mg-α'

No.	Sample	a(Å)	c(Å)	V(Å^3)
1	BCM24	7.7980(5)	5.6661(5)	298.39
2	BCM33[10]	7.8022(7)	5.6652(6)	298.66
3	BCM42	7.8050(6)	5.6765(7)	299.43
4	CCM37	7.8180(4)	5.6782(4)	300.56
5	CCM55[10]	7.8277(5)	5.6876(6)	301.80
6	CCM73	7.8286(4)	5.6925(6)	302.14

The densification of Si_3N_4-based ceramics mainly depends on the liquid phase produced by the surface SiO_2 on Si_3N_4 powder and the oxide additives. The formation of α' is also through dissolve and precipitation which in turn requires a certain amount of liquid phase. Therefore, the existence of very small amount of unreacted α-Si_3N_4 in the samples for $x = 0.6$ compositions could be attributed to the fact of less liquid phase formed during sintering for low x compositions. In our previous work [9], it was found that for the compositions with x more than 1.0, AlN-polytypoid phase 21R occurred in Ca-α'. It is also possible to form Mg-containing AlN-polytypoid phase in Ca,Mg-α', because magnesium can be incorporated into sialon system to form polytypoid phase, especially for the compositions with x equal to or more than 1.0 [5]. In the present work, Mg-containing AlN-polytypoid phase was detected with the different content in most of samples, which increased with the increase of x values, as listed in Table I. The trace amount of Mg-containing AlN-polytypoid found in BCM24 can be understood since this composition contains relatively more content of Mg than BCM42. The similar formation trend of Mg AlN-polytypoid for $x = 1.0$ compositions was caused by the same reason.

3.2. Cell dimensions

The cell dimensions of Ca,Mg-α' samples hot pressed at 1750°C are listed in Table II. For comparison, the lattice parameters of BCM33 and CCM55 (same atomic ratios of Ca to Mg to be 0.3 : 0.3 and 0.5 : 0.5 respectively) [10] are also given in the Table. It can be seen that cell dimensions of α' increase with increasing x values of the compositions. The lattice expansion of α' phase also occurred in Ca-α', which was mainly caused by the substitution of Si-N by Al-N and consequently the increases in cell dimensions of Ca-α' were depending on the x values of the compositions [9]. On the other hand, it was found in the present work that with increasing atomic ratios of Ca to Mg for the same x value ($x = 0.6$), the lattice parameters of α' phase became larger, implying more Ca^{++} being incorporated into α' structure. The similar trend was obtained for CCM37, CCM55 and CCM73 as the lattice parameters of α' phase increased with increase of amount of Ca for $x = 1.0$ compositions.

In Ca-α' work [9], the relationship between the expansion of cell dimensions of α' and actual x value was established and figured out. As Ca^{++} is the main cation to enter α' structure in Ca,Mg-α', this relationship could be roughly used to estimate the amount of cation in α'. To simplify, the cell volumes of α' were used in the relationship instead of cell axis a and c. As shown in Fig. 1, the solid circles in the figure represent the cell volumes of Ca-α' for the different actual compositions. For the compositions with the atomic ratio of Ca to (Ca+Mg) to be around 0.3, i.e. BCM24 and CCM37, the corresponding actual x values obtained from Fig. 1 were about 0.31 and 0.43. These values were about 55% and 42% higher than the nominal ones 0.2 and 0.3 (amount of Ca) for compositions BCM24 and CCM37 respectively. On the other hand, when the atomic ratio

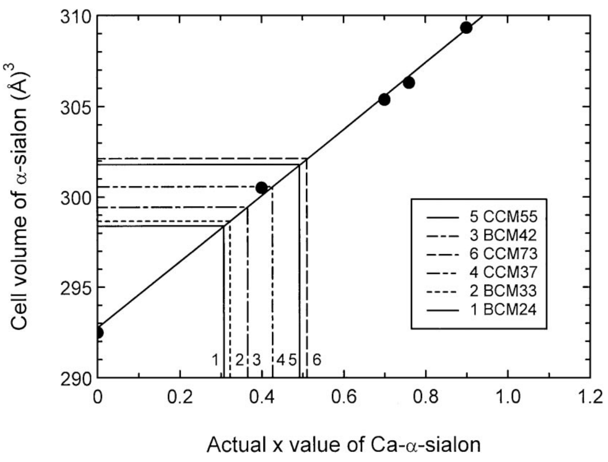
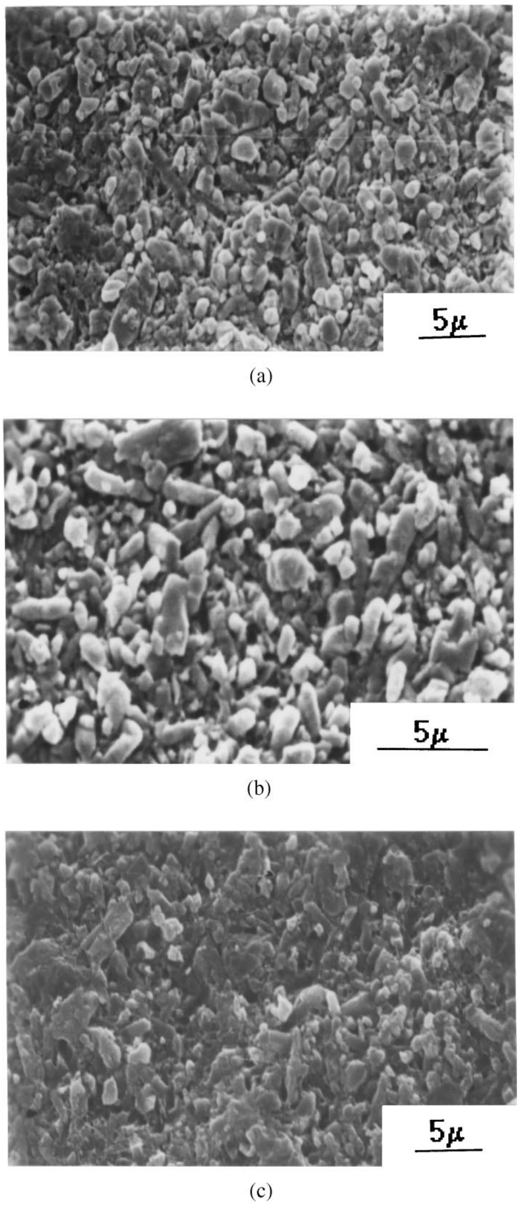


Figure 1 Cell volume vs. actual x value of Ca-α' [9] and the results used for Ca,Mg-α'.

of Ca to Mg was equal, the estimated actual x values of 0.32 and 0.49, obtained from Fig. 1 for BCM33 and BCM55 respectively, were very close to the nominal compositions. With increasing the atomic ratio of Ca to Mg, the actual numbers of cation to enter α' were lower than nominal values, especially for CCM73, as the values obtained by Fig. 1 to be around 0.37 and 0.51 for BCM42 and CCM73 respectively. This was attributed to the less liquid formed during sintering in BCM42 and CCM73, which can be illustrated by the lower densities of BCM42 and CCM73 than BCM24 and CCM37 respectively. As mentioned above that for the compositions with lower atomic ratios of Ca to Mg, like BCM24 and CCM37, the increment in lattice parameters of α' was obvious. Consequently, the estimated actual x values were much higher than the normal value for cation Ca^{++} in the compositions. It was therefore considered that the cation, which was actually incorporated into α', were composed of most of Ca^{++} and part of Mg^{++}. The results also imply that this kind of composition with low atomic ratio of Ca to Mg is beneficial to improve the sintering ability of the materials and to absorb more cations into α' structure.

3.3. Microstructure and mechanical properties

The microstructures of the etched surfaces of BCM24 and BCM42 were observed as shown in Fig. 2a and b. It can be seen from the figures that most of grains have the morphology of elongated shape. As the phase compositions in two samples are mainly composed of α' phase, the elongated morphology in the materials belongs to α' grains. In the resent years, α' grain with elongated morphology has been reported by several literatures [9, 11–16] and it was found that in the M-Si-Al-O-N (M = rare earth and Ca) systems, the liquid phase promoted the formation of elongated α', which meant that α' with elongated morphology occurred easily for the compositions with high x value lying on the line between Si_3N_4 and $CaO:3AlN$ or $R_2O_3:9AlN$ (R = rare earth). The microstructure showing in the present work indicated that α' grain could develop into aciculate morphology in Ca,Mg-α', even like BCM24 and BCM42 with a relatively low x value 0.6. No obvious difference in morphology of α' grain was observed between BCM24 and BCM42. The longest α' grain observed was around 5 μm in length, however, most of elongated grains were between 2–4 μm with aspect ratio of 2–3 as seen in Fig. 2. The fractured surface of BCM24 was observed (see Fig. 2c) and the photograph also showed the elongated morphology and pulled out of α' grains as the fractured samples were obtained after the measurement of flexural strength.



(a)

(b)

(c)

Figure 2 SEM micrographs of (a) BCM24 and (b) BCM42, both photos were taken on etched surfaces, (c) fractured surface of BCM24.

The mechanical properties of Ca,Mg-α' at 1750°C are listed in Table III. As indicated, the hardness was

TABLE III Mechanical properties of Ca,Mg-α' hot pressed at 1750°C/1 h

Sample	Hv_{10} (GPa)	K_{1c} (MPa·m$^{1/2}$)	σ_f (MPa)
BCM24	18.6	6.1	590
BCM42	18.0	5.7	—[a]
CCM37	17.7	5.8	—
CCM73	18.1	5.4	—

[a] Not measured.

relatively higher for the compositions with low x value than high x value, which could be considered as a result of the decrease of liquid phase for the compositions with low x value. On the other hand, toughness did not obey the general trend as in Ca- and Ca,Mg-α' [5, 9], in which toughness increased with the composition shift towards high x value because of more elongated α' and AlN-polytypoid contained. Among BCM24, BCM42, CCM37 and CCM73 samples, BCM24 possessed the highest toughness 6.1 MPa·m$^{1/2}$ as seen from Table III, which was attributed to the contribution of better sintering ability and toughening of elongated α' grains. The flexural strength of BCM24 was also measured and the corresponding value was 590 MPa. The results indicated that composition BCM24 had the best combination of fracture toughness and hardness. It also shows that the best way to increase the fracture toughness is not through increasing liquid phase, which will sacrifice the other properties. It is believed that to optimize compositions so proper as to make material a better sintering ability and less amount of grain boundary for Ca,Mg-α' should be a best way. It is also expected that the mechanical properties of multi-cation α' could be tailored through the adjustment of the molar ratios of oxides in the starting compositions.

4. Conclusion

Multi-cation α-Sialons ceramics containing calcium and magnesium for the composition ($(Ca,Mg)_x Si_{12-3x} Al_{3x} O_x N_{16-x,}$), where the atomic ratios of Ca to Mg equal to 0.2 : 0.4, 0.4 : 0.2 for $x = 0.6$ and 0.3 : 0.7, 0.7 : 0.3 for $x = 1.0$ respectively, were fabricated by hot-pressing. For the compositions with $x = 0.6$, the crystalline phases of the samples were mainly composed of α' phase. With high x value, Mg AlN-polytypoid phase appeared, whose content increased with increase of x value or atomic ratio of Mg to Ca under the same compositions. The results of cell dimensions indicated both x values and atomic ratios of Ca to Mg did have effect on the lattice parameters of multi-cation Ca,Mg-α'. The higher x values and atomic ratios of Ca to Mg, the larger lattice parameters of α'. For the compositions with low atomic ratios of Ca to Mg, like BCM24 and CCM37, the cations, which were actually incorporated in α' structure, were composed of most of Ca^{++} and part of Mg^{++}. Furthermore, this kind of compositions are beneficial to improve the sintering ability of the materials and to absorb more cations into α' structure. It was found by microstructural observation that most of α' grains developed into aciculate morphology even for the compositions with relatively low x (to be 0.6) in multi-cation Ca,Mg-α'. An α' ceramic with combined high hardness 18.6 GPa and toughness 6.1 MPa·m$^{1/2}$ was obtained. It shows that the best way to increase the fracture toughness is not through increasing liquid phase, which will sacrifice the other properties, and should be to optimize compositions so proper as to make a better sintering ability and less amount of grain boundary in Ca,Mg-α'. It is also expected that the mechanical properties of multi-cation α' could be tailored through the adjustment of the molar ratios of oxides in the starting compositions.

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