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Effect of dual elements (Ca, Mg) and (Ca, La) on cell dimensions of multi-cation α-sialons

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Abstract

The lattice parameters of multi-cation α-sialons containing Ca and Mg have been studied for the compositions $M_xSi_{12-3n}Al_{3-n}O_nN_{16-n}$ ($M = 0.5Ca + 0.5Mg$) with x ranging from 0.3 to 1.4 by using a Guinier–Hägg camera film data. The results indicated that the cell dimensions of Ca, Mg-α-sialon were obviously smaller than that of Ca-α-sialon with the same compositions. The EDAX analysis showed that the contents of Ca in the grains were much higher than Mg and the average value of Ca contents could be close to the one in nominal composition, implying that Ca was easily "pushed" towards α-sialon structure in multi-cation α-sialons case. Based on these results, α-sialon ceramics using 70%Ca + 30%La as additives were prepared. The lattice parameters of the α-sialons, in which 30%Ca were replaced by La as additives, were close to the single-cation Ca-α-sialon under the same compositions, indicating that most of Ca were incorporated in α-sialon because La cannot be absorbed to α-sialon structure. The advantage of using additives Ca combined with La to form α-sialon was discussed in the paper. Consequently, one composition of α-sialon with Ca and La as additives possessing hardness H_{v10} and fracture toughness K_{1c} to be 18.5 GPa and 5.5 MPa $m^{1/2}$, respectively, was obtained.

Keywords: CaO; Lattice parameter; La_2O_3; MgO; Sialon

1. Introduction

It has been well known that α-sialon[1] (abbreviated as α′) ceramics, 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 is the valency of the cation), possesses some good properties, such as high hardness, good oxidation and creep resistance. During the sintering of α′, 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 also 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. However, the higher nitrogen content in the α′ composition usually makes the material difficult to achieve full densification. To improve the sintering ability, the increase of amount of additives in addition to α′ composition is an available way. On the other hand, it will also result in the increase of the amount of grain boundary phase after sintering, thus deteriorating mechanical properties of the materials at high temperature. It can be understood that the densification of multi-cation α′ materials would be more easily to achieve in comparison with single-cation α′ materials because the dual cations materials, for example, result in a lower eutectic temperature. In fact, some investigations dealing with dual cation α′ materials have been reported within the last decade.[2–4] To alleviate the sintering problem of Ca-α′, dual cations, Ca^{++} and Mg^{++}, were used to form α′ ceramics in our previous work and the formation behavior of multi-cation α-sialons containing calcium and magnesium was reported recently.[5] The results indicated that by use of duplex metal oxide (CaO/MgO), instead of CaO, as additives to form α′, the material possessed an improved sintering ability and the better mechanical properties.

Theoretically speaking, the formation of α′ is a process of cleaning the grain boundary of the material.

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However, since some of liquid phase would still remain as glassy phase at the grain boundary of α′ after cooling down, the content of cations, which are actually entered into α′ structure, would be less than the nominal value in composition. In our previous work,[6] it was found that when x was less than 1.4 (top limit of solubility of Ca-α′ [7]), about 70% of Ca^{++} in nominal composition entered into α′ structure with the remainder in grain boundary of the material. On the other hand, the absorbed cations caused the cell expansion, which increased linearly with increasing the amount of absorbed cations according to the reported results for Y-, Sm- and Ca-α′.[6,8,9] Therefore, the determination of α′ cell could provide an information of solubility of cations in α′ and reflect, to some extent, the amount of residual grain boundary in the materials.

Owing to above consideration, the variations of cell dimensions of multi-cation α′ containing Ca and Mg with the different x values were studied in the present work. Combined with EDAX analysis, a further investigation on the solubility of Ca^{++} in multi-cation Ca,Mg-α-sialons was also performed. Based on the obtained results, duplex elements Ca and La were used as additives in the formation of α′. The effect of Ca, La on cell dimensions of α′ was studied and the advantage to choose La_2O_3 as additive was also discussed in the paper. Consequently, the mechanical properties of α′ with Ca and La as additives were determined in a comparison with Ca-α′.

2. Experimental

The nominal compositions used in the present work were located on the join between Si_3N_4 and MO:3AlN [M = (Ca,Mg) or (Ca,2/3La)] with formula $M_xSi_{12-3n}Al_{3n}O_nN_{16-n}$ (x = 0.3, 0.6, 1.0 and 1.4 for M = Ca + Mg, x = 0.6 and 1.0 for M = Ca + La), where m = 2n = xv. The starting powders used were Si_3N_4 (UBE-10, Japan, 2.0 wt%O), AlN (1.3 wt%O), $CaCO_3$ (99.0%), MgO (99.0%) and La_2O_3 (99.5%). The ratio of Ca to Mg used in the compositions was 0.5:0.5. For ratio of Ca to La, 0.7:0.3 was used. The powder mixtures were milled for 1.5 h in an agate mortar under absolute alcohol. Powders were dried and then hot-pressed (20 MPa) at 1700 or 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 dissolution of $CaCO_3$. The bulk densities of the samples were measured by the Archimedes principle. The phase analysis of the prepared samples was based on X-ray diffraction data from a Guinier-Hägg camera with use of Cu $K_{\alpha 1}$ radiation and Si as the internal standard. The obtained photographs were evaluated with a computerised scanner system.[10] The determinations of unit cells of α′ were performed by means of PIRUM program [11] based on Guinier–Hägg film data. The contents of Ca, Mg in α′ were measured on the surfaces of polished samples under a SEM (KYKY2000, China) equipped with Oxford/LINK ISIS 3.00 energy dispersive spectrometers. Hardness and indentation fracture toughness of the materials were determined by using a Vickers diamond indenter under a load of 100 N.

3. Results and discussion

The nominal compositions used and phase present in the hot-pressed (1750°C) samples are listed in Table 1. For Ca,Mg-α′ compositions with x = 0.3 and 0.6, the reactions were not completed when the samples were sintered at 1750°C for 1 h as some very weak diffraction peaks of α-Si_3N_4 appeared in the XRD patterns. This is because the formation of α′ is through dissolution and precipitation which in turn requires a certain amount of liquid phase and the compositions with lower x values cause the decrease in the amount of liquid phase during sintering. The CM1 composition (x = 0.3) is located below the lowest limit of the Ca-α′ solubility region,[7,12] in which there is a two phase (α′ + β′) region. Therefore, the appearance of β′ with that composition is expected. For CM3 and CM4, the phase assembly consists of α′, as a major phase, and magnesium containing AlN-polytypoid, in which the amount of AlN-polytypoid increases slightly with higher x-value as explained in Ref. 5.

The lattice parameters of α′ phase in CM1, CM2, CM3 and CM4 samples sintering at 1700 and 1750°C

Table 1
The nominal compositions and phase present of samples hot pressed at 1750°C for 1 h

Sample no.	Nominal composition	Nominal x	Ca:Mg or Ca:La	Phase present[a]
CM1	$Ca_{0.15}Mg_{0.15}Si_{11.1}Al_{0.9}O_{0.3}N_{15.7}$	0.3	0.15:0.15	α′/s, β′/mw, α /tr
CM2	$Ca_{0.3}Mg_{0.3}Si_{10.2}Al_{1.8}O_{0.6}N_{15.4}$	0.6	0.3:0.3	α′/s, α /tr
CM3	$Ca_{0.5}Mg_{0.5}Si_{9.0}Al_{3.0}ON_{15.0}$	1.0	0.5:0.5	α′/s, Mg AlN-polytypoid/mw
CM4	$Ca_{0.7}Mg_{0.7}Si_{7.8}Al_{4.2}O_{1.4}N_{14.6}$	1.4	0.7:0.7	α′/s, Mg AlN-polytypoid/m
CL1	$Ca_{0.42}La_{0.18}Si_{9.93}Al_{2.07}O_{0.69}N_{15.31}$	0.6	0.42:0.18	α′/s
CL2	$Ca_{0.7}La_{0.3}Si_{8.55}Al_{3.45}O_{1.15}N_{14.85}$	1.0	0.7:0.3	α′/s, gehlenite/mw

[a] s = strong, m = medium, w = weak, tr = trace, β′ = β-sialon ($Si_{6-Z}Al_ZO_ZN_{8-Z}$), gehlenite = $Ca_2SiAl_2O_7$.

Table 2
The lattice parameters of α' phase in (Ca,Mg)-α' samples sintered at 1700 and 1750°C

Sample no.	a (Å)		c (Å)		V (Å)^3	
	1700°C	1750°C	1700°C	1750°C	1700°C	1750°C
CM1	7.7838 (4)	7.7842 (8)	5.6539 (3)	5.6524 (7)	296.66	296.62
CM2	7.7998 (5)	7.8022 (7)	5.6650 (5)	5.6632 (6)	298.47	298.66
CM3	7.8250 (4)	7.8277 (5)	5.6853 (6)	5.6853 (6)	301.48	301.80
CM4	7.8524 (6)	7.8548 (5)	5.7074 (9)	5.7027 (5)	304.77	304.71

Table 3
A comparison of lattice parameters between Ca-α' [6] and (Ca,Mg)-α' (1700°C/1 h)

	$x=0.3$		$x=0.6$		$x=1.0$		$x=1.4$	
	C1[6]	CM1	C2[6]	CM2	C3[6]	CM3	C4[6]	CM4
a (Å)	7.7932 (6)	7.7838 (4)	7.8163 (7)	7.7998 (5)	7.8584 (7)	7.8250 (4)	7.8914 (5)	7.8524 (6)
c (Å)	5.6652 (8)	5.6539 (3)	5.6796 (9)	5.6650 (5)	5.7098 (7)	5.6853 (6)	5.7356 (6)	5.7074 (9)
V (Å)^3	297.97	296.66	300.50	298.47	305.37	301.48	309.32	304.77
ΔV[a] (Å)^3		1.31		2.03		3.89		4.55

[a] $\Delta V = V_{\text{Ca}-\alpha'} - V_{(\text{Ca,Mg})-\alpha'}$.

are listed in Table 2. As seen from the table, the unit cells of α' from CM1 to CM4 become larger with increasing x values of compositions. On the other hand, the differences in the lattice parameters of α' between 1700 and 1750°C sintering are mostly within the standard deviations of measurements, indicating that the solubilities of cations Ca^{++} and Mg^{++} in α' structure almost remain constant with increasing sintering temperatures from 1700 to 1750°C. In order to compare the lattice parameters of Ca,Mg-α' with its single cation Ca-α' counterpart (named as C1, C2, C3 and C4 for $x=0.3$, 0.6, 1.0 and 1.4, respectively), Table 3 gives the lattice parameters for both Ca-α' and Ca,Mg-α' phases sintered at 1700°C. It can be seen that lattice parameters of Ca,Mg-α' are obviously smaller than that of Ca-α' under the same compositions, which means that the amounts of incorporated cations into α' structure become smaller when cation Ca^{++} is half replaced by Mg^{++}. Combined with the results of phase analysis, i.e. the formation of magnesium containing AlN-polytypoid phase in CM3, CM4 samples, it seems to be reasonable to reduce the solubility of Mg^{++} ion in multication Ca,Mg-α', which could result in less expansion of unit cell of α' phase. However, as the decrements of cell dimensions of α' phase occur in overall four samples as shown in Table 3, it is necessary to know the role about ratio of Ca to Mg ions entering the α' structure in multication Ca,Mg-α'. EDAX analysis was therefore used to measure the distributions of elements in α' grains. The average of ten measurement points was used as a representative value of EDAX analysis for each CaMg-α' sample (see Table 4). As seen from the table, that the total actual x values of cations entering α' structure are about half of the nominal x values when Ca^{++} is half replaced by Mg^{++}, in which around 85–90% of incorporated cations are Ca^{++}. This result is in accordance with the one obtained by TEM and EDAX for Ca,Mg-α' composition $x=1.4$ reported in our previous paper,[5] which shows that most of the added Ca^{++} and much less of Mg^{++} are incorporated into the α' structure, whereas most of the added Mg^{++} enter sialon polytypoid to form the magnesium AlN-polytypoid phase. The above results, i.e. lattice parameters and actual x values of Ca,Mg-α' phases, were also examined based on the relationships between lattice parameters of α' and actual x values obtained for Ca-α' [6] (shown in Fig. 1), as the major cation incorporated into α' structure in Ca,Mg-α' case was Ca^{++}. In Fig. 1, solid circles represent the cell volumes of Ca-α' phases under the different actual x values of compositions and the variations of cell volumes of Ca-α' with actual x values satisfy linear relation. The cell volumes of Ca,Mg-α' with the different actual x values are plotted as the empty squares in Fig. 1. It can be seen that the relationships between cell volumes of Ca,Mg-α' and the actual x values are mostly in accordance with the Ca-α' case.

Table 4
A comparison of nominal x to actual x in (Ca,Mg)-α' samples

Sample no.	Nominal		Actual	
	x	Ca:Mg (at%)	x	Ca:Mg (at%)
CM1	0.3	0.15:0.15	0.16	0.14:0.02
CM2	0.6	0.3:0.3	0.29	0.25:0.04
CM3	1.0	0.5:0.5	0.50	0.45:0.05
CM4	1.4	0.7:0.7	0.71	0.62:0.09

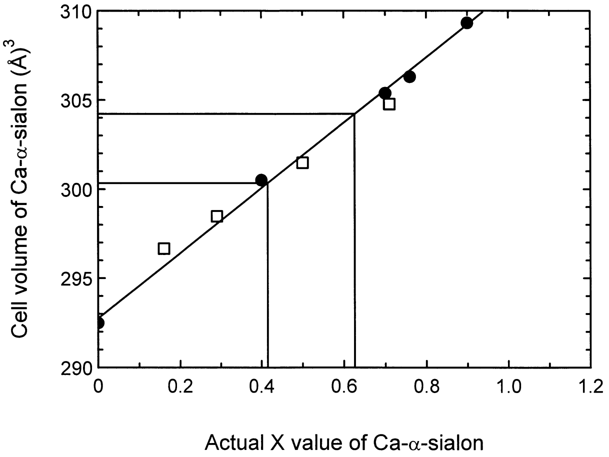

Fig.1. Cell volumes vs actual x value of Ca-α-sialon.

The above results indicate that the solubility of cations in multi-cation α′ containing Ca and Mg is decreased when Ca^{++} is half replaced by Mg^{++}. On the other hand, more Ca^{++} in Ca,Mg-α′ compositions are "pushed" towards α′ structure comparing with Ca-α′, as the solubility of Ca^{++} is increased from 70% in single cation Ca-α′ [6] to 85–90% in multi-cation Ca,Mg-α′. Based on the results, it was supposed that the use of dual elements as additives in α′ compositions, in which one element just has very low or no solubility in α′ structure, would promote the solubility of active cation in α′ phase. Therefore, rare earth element La was thought to be used as additive combined with Ca in the formation of α′ phase as it was well known that La can not be absorbed into α′ structure and the glassy phase containing La in grain boundary of α′ ceramics would possess high refractory.

The compositions used for α′ with Ca and La as additives were the same as multi-cation α′ containing Ca and Mg, i.e. $M_xSi_{12-3n}Al_{3n}O_nN_{16-n}$, in which x values were 0.6 and 1.0. Due to the results that around 70% of Ca^{++} in nominal Ca-α′ compositions were incorporated in α′ structure when x was less than 1.4,[6] 30%Ca in α′ compositions were replaced by La for samples CL1 ($x=0.6$) and CL2 ($x=1.0$) respectively (see Table 1). The bulk densities of CL1 and CL2 samples were measured to be 3.254 and 3.317 g/cm^3, respectively. The phases present in the samples are listed in Table 1. For CL1, the reaction, after hot-pressed at 1750°C for 1 h, was completed and α′ was the only present phase. For CL2, the phase assemblages consisted of α′, as a major phase, and gehlenite. The lattice parameters of α′ using Ca, La as additives are listed in Table 5. The cell dimensions of corresponding Ca-α′ phases are also given in Table 5 for comparison. It is noticed that the cell volumes of α′ using Ca,La as additives are very close to the ones of Ca-α′ with the same x values, especially for $x=0.6$. As about 70% of Ca in the nominal compositions are entered into α′ in single cation Ca-α′,[6] the similarity in cell dimensions of α′ between single cation Ca and multi-cations Ca and La implies that most of Ca in the compositions of CL1 and CL2 are absorbed to form α′, especially for CL1. The cell volumes of α′ in CL1 and CL2 samples are plotted as horizontal lines in Fig. 1 and the corresponding actual x values of α′ phase are obtained by Fig. 1 to be about 0.41 and 0.62 for CL1 and CL2 respectively. As the nominal numbers of cation Ca^{++} in CL1 and CL2 are 0.42 and 0.7, respectively, the actual amount of Ca entering α′ structure are very close to nominal ones. It is understood that small amount of Ca in CL2 sample are consumed to form gehlenite phase, which makes the actual x value of Ca less than the nominal one in CL2.

Mechanical properties of CL1 and CL2 samples are measured and the results are listed in Table 5. The hardness values of CL1 and CL2 are 18.5 and 16.7 GPa, respectively. The fracture toughness of CL samples are 5.5 and 4.9 MPa m$^{1/2}$ for $x=0.6$ and 1.0, respectively. The decrement in hardness and fracture toughness in CL2 sample compared with CL1 are considered to be the results of the increase of quantity of liquid phase in the material and the existence of gehlenite phase. It is noticed however that the fracture toughness of CL1 sample reaches 5.5 MPa m$^{1/2}$ with a hardness of 18.5 GPa. The combined mechanical properties of CL1 are better than its counterpart[13] (see Table 5). It is also expected that CL1 ceramics would possess good mechanical properties at high temperature as glassy phase in the grain boundary of CL1 mainly consists of La, Si,Al,O,N. Therefore, α′ ceramics using CaO and La_2O_3 as additives is considered to be a promising material and more work is worthy to be carried out.

Table 5
The lattice parameters and mechanical properties of α′ using Ca,La as additives hot-pressed at 1750°C for 1 h

Sample no.	Cell dimension			Mechanical property	
	a (Å)	b (Å)	V (Å)^3	H_{v10} (GPa)	K_{1c} (MPa m$^{1/2}$)
CL1	7.8121 (5)	5.6823 (6)	300.33	18.48	5.5
CL2	7.8470 (5)	5.7049 (5)	304.22	16.67	4.9
C2	7.8185 (13)[6]	5.6752 (8)[6]	300.44[6]	18.79[13]	4.7[13]
C3	7.8532 (7)[6]	5.7185 (6)[6]	305.42[6]	17.94[13]	5.3[13]

4. Conclusion

The cell dimensions of multi-cation α-sialons containing calcium and magnesium were obviously smaller than that of Ca-α-sialon with the same compositions. EDAX analysis indicated that more Ca were "pushed" towards α-sialon structure in multi-cation α-sialons comparing with single cation Ca-α-sialon, as the solubility of Ca was increased from 70% in Ca-α-sialon to 85–90% in Ca,Mg-α-sialons. The lattice parameters of α′ using 70%Ca + 30%La as additives were very close to the ones of Ca-α′ with the same x values in α′ compositions, especially for $x = 0.6$. The similar values of cell dimensions indicated that the Ca amounts incorporated in α′ phases in both cases were similar and most of Ca in the compositions of CL1 and CL2 were absorbed to form α′ because La cannot be entered to α′ structure. The results obtained in the present work imply that the use of dual elements as additives in α′ compositions, in which one element just has very low or no solubility in α′ structure, would promote the solubility of active cation in α′ phase. The mechanical properties of one composition of Ca,La-α-sialon with hardness H_{v10} and fracture toughness K_{1c} were 18.5 GPa and 5.5 MPa m$^{1/2}$ were obtained in this work.

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References

1. Hampshire, S., Park, H. K., Thompson, D. P. and Jack, K. H., α′-sialon ceramics. *Nature*, 1978, **274**, 880–882.
2. Redington, M. and Hampshire, S., Multi-cation α-sialons. *Br. Ceram. Proc.*, 1992, **49**, 175–190.
3. Huang, Z. K., Jiang, Y. Z. and Tien, T. Y., Formation of α-sialons with dual modifying cations (Li + Y and Ca + Y). *J. Mater. Sci. Lett.*, 1997, **16**, 747–751.
4. Hwang, C. J., Susnitzky, D. W. and Beaman, D. R., Preparation of multication α-sialon containing strontium. *J. Am. Ceram. Soc.*, 1995, **78**, 588–592.
5. Wang, P. L., Zhang, C., Sun, W. Y. and Yan, D. S., Formation behavior of multi-cation α-sialons containing calcium and magnesium. *Materials Letters*, 1999, **38**, 178–185.
6. Wang, P. L., Zhang, C., Sun, W. Y. and Yan, D. S., Characteristics of Ca-α-sialon–phase formation, microstructure and mechanical properties. *J. Eur. Ceram. Soc.*, 1999, **19**, 553–560.
7. Huang, Z. K., Sun, W. Y. and Yan, D. S., Phase relation of the Si_3N_4–AlN–CaO system. *J. Mater. Sci. Lett.*, 1985, **4**, 255–259.
8. Sun, W. Y., Tien, T. Y. and Yen, T. S., Solubility limits of α′-sialon solid solutions in the system Si,Al,Y/N,O. *J. Am. Ceram. Soc.*, 1991, **74**, 2547–2550.
9. Shen, Z. J., Ekström, T. and Nygren, M., Temperature stability of samarium-doped α-sialon ceramics. *J. Eur. Ceram. Soc.*, 1996, **16**, 43–53.
10. Johansson, K. E., Palm, T. and Werner, P.-E., An automatic microdensitometer for x-ray powder diffraction photographs. *J. Phys. E.: Sci. Instrum.*, 1980, **13**, 1289–1291.
11. Werner, P. E., A fortran program for least-squares refinement of crystal-structure cell dimensions. *Arkiv fur Kemi.*, 1964, **31**, 513–516.
12. Hewett, C. L., Cheng, Y. B., Muddle, B. C. and Trigg, M. B., Phase relationships and related microstructural observations in the Ca–Si–Al–O–N system. *J. Am. Ceram. Soc.*, 1998, **81**, 1781–1788.
13. Li, Y. W., Wang, P. L., Cheng, Y. B. and Yan, D. S., Microstructure and property anisotropy of hot-pressed Ca-α-sialon. *J. Mater. Sci. Letters*, in press.