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Implications of kinetically promoted formation of metastable α-sialon phases

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Abstract

α-Sialon ceramics are interesting materials, because alone or together with β-sialon they can form in-situ reinforced microstructures which offer the best combinations of strength, hardness and toughness. At temperature above 1200°C, the thermal stability of α-sialon phases has been debated since 1992, however, and it has been discussed if any α-sialon phase can be formed in Ce-, La-, Eu- and Sr-doped sialon systems. Using a novel rapid densification process named spark plasma sintering (SPS), which allows preparation of fully dense compacts of sialon ceramics within a few minutes, we here show that α-sialon phases are initially formed in these systems and that subsequent in situ and ex situ post heat-treatment results in a decomposition of the α-sialon phase. These observations show that cations with a radius larger than 1 Å may stabilize the α-sialon phase, which contrasts with previous findings. The thermal stability of these α-sialon phases is strongly dependent on the kinetics of the reactions occurring when one approaches thermodynamic equilibrium. The findings might also have bearing on other sialon systems than those studied here. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Silicon nitride occurs as three polymorphs. The α- and β-Si_3N_4 modifications are well known, both having hexagonal structures, while the cubic modification, having a spinel structure, was discovered recently.[1] Although both α- and β-Si_3N_4 exist in air at ambient pressure and temperature, it seems to be accepted that the β form is thermodynamically more stable than α at temperatures exceeding 1400°C. The constraints of the α→β–Si_3N_4 transformation at temperatures below 1400°C are thus believed to be kinetic rather than thermodynamic. The presence of a liquid facilitates this structural transformation via a solution–precipitation mechanism.[2,3]

A solid solution phase isostructural with α-Si_3N_4, formed by substituting Al and O for Si and N, respectively, and simultaneously incorporating metal cations (M) into the interstices present in the α-Si_3N_4 structure, was discovered in 1978.[4] This phase, named α-sialon, has the formula $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, and it was regarded as a thermodynamically stable phase till the early 1990s when Mandal et al. reported that the α-sialon phase in certain systems is stable only at high temperatures (typically $T > 1550°C$), whereas upon post-heat treatment at lower temperature it decomposes to the β-sialon modification $Si_{6-z}Al_zO_zN_{8-z}$, isostructural with β-Si_3N_4, and other phases.[5] Since then, a number of studies have been carried out with the aim to elucidate the thermal stability of the α-sialon phase in different sialon systems and at temperatures ranging from 1000 to 1900°C. Much of the previous work describes how the α-sialon decomposition takes place, and what main factors affect the decomposition kinetics, while less attention has been paid to the driving force for the decomposition reactions (Ref. 6 and the references therein). Very recently however, work carried out individually by Rosenflanz and Chen and by us, indicates that α-sialon may persist as a metastable phase only in systems where thermodynamic equilibrium varies with temperature and when the true thermodynamic equilibrium is kinetically retarded.[7,8] Moreover, in our previous work we have noticed that α-sialon may persist as a metastable phase even at temperatures above 1600°C in an Nd-doped system, when the formation of a nitrogen-

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rich so-called JEM phase, $NdAl(Si_{6-z}Al_z)N_{10-z}O_z$ ($z \approx 1$), is kinetically retarded.[8]

JEM analogues are most easily formed in Ce- and La-doped sialon systems, where the formation of α-sialon phase has been debated and where, accordingly, the established phase compatibility relationships seem to differ from those established in Y-doped and other rare-earth systems.[9–11] The finding that α-sialon may form as a transient metastable phase when the formation of a thermodynamically stable phase such as JEM is kinetically retarded, encouraged us to a test if a metastable transient α-sialon phase is formed prior to the JEM phase in Ce- and La-doped sialon systems and prior to the S-phase, $Sr(Eu)2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$), another new nitrogen-rich phase identified by us recently, in Eu- and Sr-doped systems.[12,13]

SPS is a newly developed sintering process, in which the precursor powders are pressed uniaxially in a carbon die, and an on-off pulsed DC current is simultaneously applied. The current passes through both the carbon pressure-die and the sample, which is therefore heated both from the outside and the inside so that very fast heating rates can be applied (up to 600°C min^{-1}). In addition to heat and pressure this process utilizes the self-heating action caused by spark discharge between the particles occurring in the initial stage of the current-voltage pulse. The use of an on-off pulsed DC current also implies fast cooling of the formed inter-particle bonding and a dispersed movement of the discharge points. These processes thus promotes transfer of material and makes rapid densification of the powder compact possible at low temperatures and short holding times.[14]

2. Experimental

Four powder precursors, with nominal compositions $Ce_{0.4}Si_{10.2}Al_{1.8}O_{0.6}N_{15.4}$, $La_{0.4}Si_{10.2}Al_{1.8}O_{0.6}N_{15.4}$, $Eu_{0.48}Si_{8.5}Al_{3.5}O_{1.3}N_{14.7}$ and $Sr_{0.4}Si_{10}Al_2O_{1.2}N_{14.8}$, were prepared by ball milling of appropriate mixtures of α-Si_3N_4, AlN, and CeO_2, La_2O_3, Eu_2O_3 and $SrCO_3$ powders. The compacts were then placed in a cylindrical carbon die with an inner diameter of 20 mm, and were compacted in a spark-plasma sintering apparatus, Dr. Sinter 1050 (Sumitomo Coal Mining Co., Japan), using a pressure of 50 MPa. The sintering temperature was set to 1700°C, the heating rate to 200°C/min, and the holding time to 0 or 5 min. The shrinkage and shrinkage rate during the sintering process were recorded, and the obtained data were corrected for the thermal expansion of the graphite punches. The set-up allows a cooling rate of 350°C/min in the temperature range 1700–1100°C. The samples densified at 1700°C without any holding time were post heat-treated (HT) in a graphite furnace at 1700°C for 6 h and then quenched with a cooling rate of 300°C/min. For comparison, the same powder mixtures were also compacted using a standard hot-pressing (HP) procedure at 1800°C for 2 h. The resulting materials were characterized by their X-ray powder diffractograms (XPRD), and their microstructures were studied in a scanning electron microscope (SEM) and a transmission electron microscope (TEM), each equipped with an energy-dispersive X-ray spectroscopy microanalysis facility (EDS).

3. Results and discussion

The obtained shrinkage curves are shown in Fig. 1. They reveal that the shrinkage takes place within a rather limited temperature range; fully compacted samples were obtained at 1590°C for Ce-, 1620°C for La- and Eu-, and 1670°C for Sr-doped samples, respectively.

The X-ray powder diffraction patterns of the Ce-doped samples are shown in Fig. 2. The phases present, their α/(α + β) ratio, and the unit cell dimensions of the α-sialon phases formed in all samples are listed in Table 1. The main phases formed in the SPSed samples with zero holding time are: α-sialon, small amounts of β-sialon and the 21R polytypoid phase, $SiAl_6O_2N_6$; and in the Sr(Eu)-containing samples the polytypoid phase (P) of the composition $Sr(Eu)Si_9Al_{19}ON_{31}$.[15] Some of these samples contain small amounts of unreacted α-Si_3N_4 as

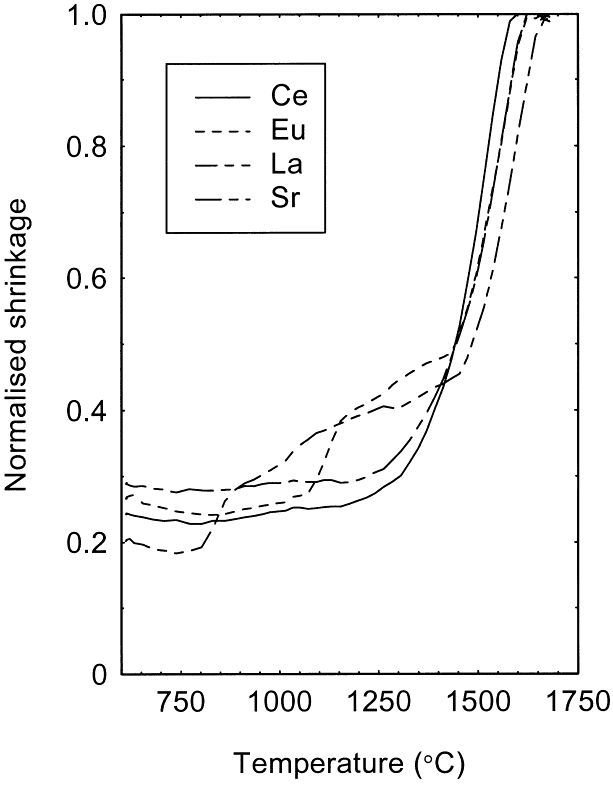

Fig. 1. Normalized shrinkage curves recorded during SPS sintering at a rate of 200 min up to 1700°C.

indicated by the X-ray diffraction peaks of the α-sialon phase having shoulders at positions expected for α-Si_3N_4. The observed lattice expansions of La- and Sr-doped α-sialons are smaller than those of Ce- and Eu-doped ones. In fact, their compositions correspond to $La_{0.12}Si_{11.24}Al_{0.76}O_{0.4}N_{15.6}$ and $Sr_{0.35}Si_{11.1}Al_{0.9}O_{0.2}N_{15.8}$, respectively, according to the EDS determination in TEM mode, which is much closer to Si_3N_4 than most of the α-sialon phases observed previously.[16] The phases formed are also clearly distinguishable in the SEM micrographs recorded in back-scattered electron mode, which are given in Figs. 3 and 4. Together with the X-ray findings, these micrographs provide convincing evidence that the α-sialon phase is formed in the SPSed samples, but not the JEM and S phases. Thus the formation of Ce-, La-, Eu- and Sr-doped α-sialon phases are kinetically promoted. As in this case the sintering procedure is finished in a very short time, it is assumed that long-distance mass diffusion is restricted, implying that the α-sialon and ploytypoid phases are formed locally and that grains of the starting materials α-Si_3N_4 and AlN may serve as nucleation sites for these phases.

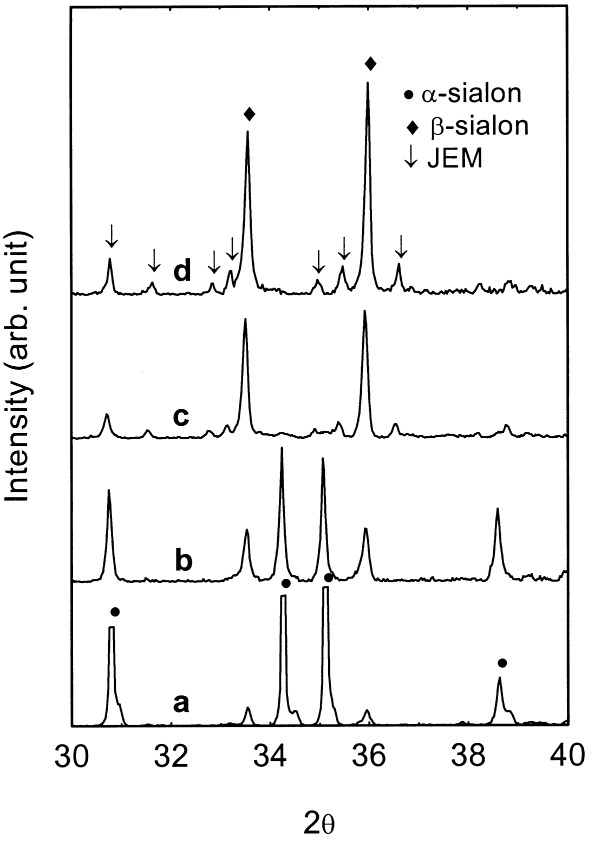

Fig. 2. The X-ray powder diffraction patterns of the Ce-doped sialon samples, after being SPSed at 1700°C with (a) no and (b) 5 min holding time, and (c) being post heat-treated at 1700°C for 6 h, as well as (d) being hot-pressed at 1800°C for 2 h.

The small amount of residual α-Si_3N_4 disappears and much more β-sialon phase is formed after holding at 1700°C for 5 min, but the JEM or S-phases are still absent. Post heat-treatment at 1700°C for 6 h decreased the amount of α-sialon phase substantially, or removed it completely, and JEM, S and other phases were formed. To a great extent the X-ray powder patterns of these samples mimic those obtained from the samples prepared by hot-pressing at 1800°C for 2 h, given in Table 1. These findings suggest that at least in these cases α-sialon in part acts as a transient phase, i.e. it forms in the early stage of the sintering process and decomposes when the system approaches equilibrium, most likely represented by the phase assemblies present in the samples hot-pressed at 1800°C for 2 h.

Based on previous experimental evidence, it has been assumed that there is an upper limit of ≈1Å for the radius of the M-cations to be accommodated in the α-sialon structure.[4,17] The assumption is difficult to understand, because the interstices where the M-cations are expected to reside are much larger, e.g. ≈2.59 Å,[18,19]

Table 1
Observed formation of α-sialon phases, and their cell parameters

	Sintering conditions	Phase assemblies	α/(α + β)[a] (%)	α-sialon unit cell	
				a (Å)	c (Å)
Ce-doped	SPS 1700°C/0 min	α(s)β(w),21R(w)	90	7.7943	5.6656
	SPS 1700°C/5 min	α(s),β(m),21R(w)	64	7.7944	5.6692
	HP 1800°C/2 h	β(s),JEM(m),21R(w)	0		
La-Doped	SPS 1700°C/0 min	α(s),β(m),21R(w)	75	7.7587	5.6259
	SPS 1700°C/5 min	α(w),β(s),21R(w)	22	7.766	5.628
	HP 1800°C/2 h	β(s),JEM(m),21R(w)	0		
Eu-doped	SPS 1700°C/0 min	α(s)β(w),P(m)	89	7.7987	5.6692
	SPS 1700°C/5 min	α(s)β(w),P(m)	78	7.8001	5.6692
	HP 1800°C/2 h	α(s),β(s),S(s),P(s)	57	7.7872	5.6589
Sr-doped	SPS 1700°C/0 min	α(s),β(w),P(m)	84	7.7569	5.6249
	SPS 1700°C/5 min	α(m),β(s),P(m)	41	7.7614	5.6310
	HP 1800°C/2 h	α(m),β(s),S(s),P(m)	44	7.7647	5.6443

[a] X-ray intensities: s = strong; m = medium; w = weak; α: α-sialon; β: β-sialon; 21R: $SiAl_6O_2N_6$; JEM: Ce(La)$Si_5Al_2ON_9$; S: Sr(Eu)$AlSi_5O_2N_7$; P: Sr(Eu)$Si_9Al_{19}ON_{31}$.

and the evidence here reported for large amounts of α-sialon forming in samples doped with Ce-, La-, Eu- and Sr contradicts it. Therefore, it seems that the stability of the α-sialon phase in the various systems studied here depends more on whether the phase diagrams contain thermodynamically more stable nitrogen-rich M^{n+}-containing phases with compositions close to the M-doped α-sialon phase, e. g. the JEM-, S- and P-phases, rather than on the ionic radius of the compensating M-cations that occupy the interstices.

These findings might also have a bearing on sialon systems other than the Ce-, La-, Eu- and Sr-doped ones studied here. Firstly, it is no longer astonishing that M–M′-doped α-sialon phases can be prepared with M = an ion with radius < 1 Å and M′ = an ion with radius > 1 Å.[17] It is also quite obvious that the thermal stability of these M–M′-doped α-sialon phases are different from the M′-doped α-sialon phases, since the overall composition of the samples is changed and thus also the phase assemblies at equilibrium. Secondly, the technical implication of these findings seems to be the following: In order to be able to prepare an α or α/β sialon compact which is thermally stable at temperatures above 1200°C, one has to select a sialon system containing none or as few as possible stable nitrogen-rich M^{n+}-containing phases with compositions close to the M-doped α-sialon phase. From this point of view the Yb-doped sialon system seems to be most promising,

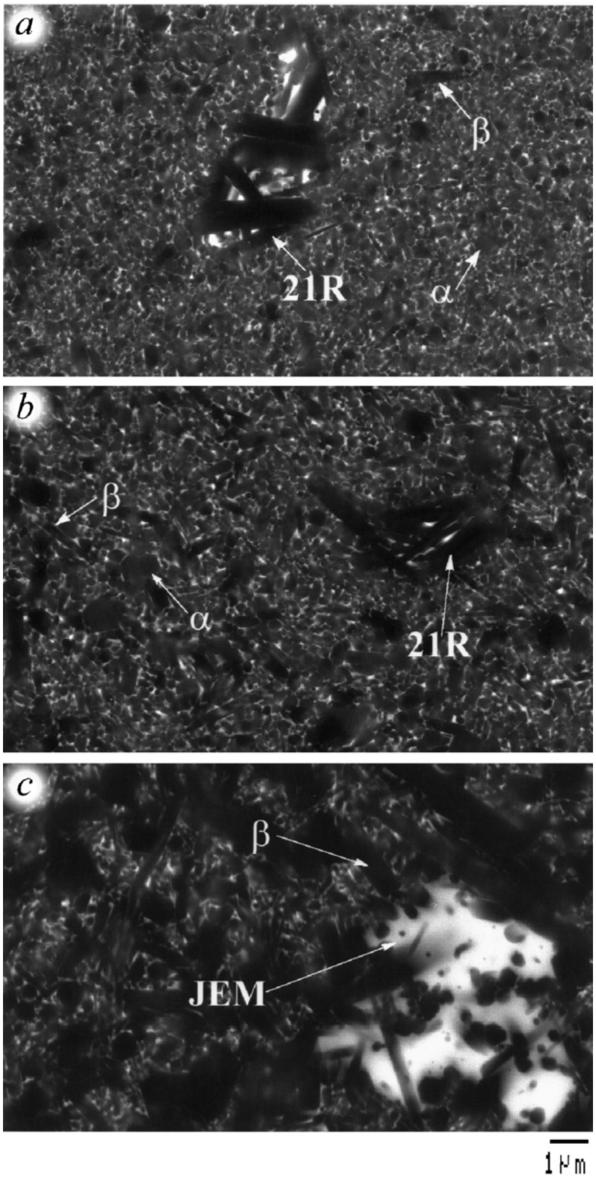

Fig. 3. Back-scattered electron scanning micrographs showing the microstructures of the Ce-doped sialon samples after being SPSed at 1700°C with (a) no and (b) 5 min holding time, and (c) being post heat-treated at 1700°C for 6 h.

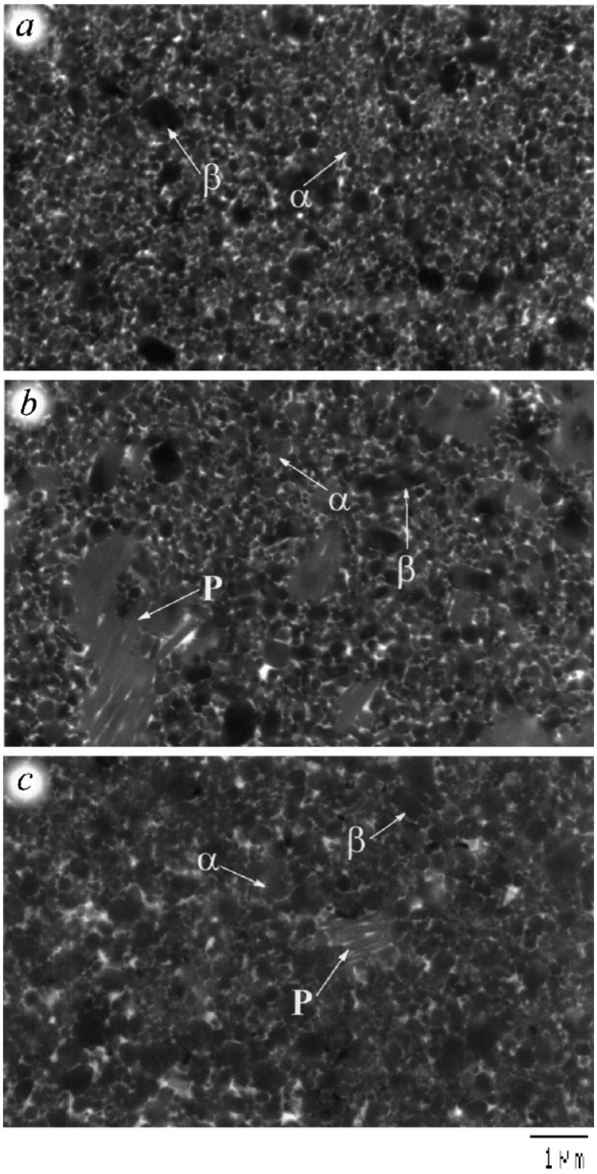

Fig. 4. Back-scattered electron scanning micrographs showing the formation of α-sialon phase after being SPSed at 1700°C without holding in La-(a), Eu-(b), and Sr-(c) doped samples.

and if one can avoid the formation of a nitrogen-rich melilite phase in the Y-doped sialon system, yttrium-stabilized sialon ceramics can also become interesting for high-temperature applications.

4. Conclusions

The spark plasma sintering technique was successfully applied to compacted sialon based ceramics in very short times. This process thus provides us with a new way to follow the initial phase transformations in sialon systems and should also be useful for investigating the transformation sequences and reaction kinetics in systems other than the one studied here. The finding that a number of metastable α-sialon phases that contains cations with a radius larger than 1 Å, e.g. Ce, La, Eu and Sr, can be obtained by a fast sintering and cooling process as the one applied here, firmly demonstrate that the stability of the α-sialon phase depends more on whether the appropriate phase diagrams contain thermodynamically more stable nitrogen-rich M^{n+}-containing phases with compositions close to the M-doped α-sialon phase, e.g. the JEM-, S- and P-phases, rather than on the ionic radius of the compensating M-cations that occupy the interstices present in the α-sialon structure. As the α-sialon phase in a sintered material seldom exists as an isolated phase, it is of immediate technical importance to select an M-compensative component which preferentially yields none or as few as possible stable nitrogen-rich M^{n+}-containing phases with compositions close to the M-doped α-sialon phase to minimize competing reactions and thus ensure that the α-sialon phase is stable over a wide temperature range.

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