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Thermal expansion coefficient of Y-α′-sialon

T. OKAMOTO, Y. UKYO
Toyota Central Research and Development Labs., Inc., Nagakute-cho, Aichi-gun, Aichi 480-11 Japan

A sialon composite composed of Y-α′-sialon and β′-sialon has been fabricated by hot pressing mixtures of Si_3N_4, Y_2O_3 and AlN powders. Thermal expansion coefficients of the Y-α′-sialon and β′-sialon were determined by the high-temperature X-ray diffraction technique. The thermal expansion coefficient of Y-α′-sialon depended on the composition, being minimum at $x = 0.3$ in the formula $Y_x(Si_{12-4.5x}, Al_{4.5x})(O_{1.5x}, N_{16-1.5x})$. The coefficient of β′-sialon increased with increasing lattice constant, that is, the z value in the formula $Si_{6-z}Al_zO_zN_{8-z}$. The thermal expansion coefficient of sialon composites determined by a differential dilatometer increased with increasing amount of Y-α′-sialon.

1. Introduction

In the Y–Si–Al–O–N system, α′-sialon containing yttrium (Y-α′-sialon) is formed in a limited range [1]. Y-α′-sialon is obtained by sintering mixtures of Si_3N_4, Y_2O_3 and AlN powders [2]. In this case, Y-α′-sialon is generated according to the following reaction

$$(4.5 - 1.5x)Si_3N_4 + 0.5x(Y_2O_3 + 9AlN) = Y_x(Si_{12-4.5x}, Al_{4.5x})(O_{1.5x}, N_{16-1.5x}) \quad (1)$$

where, Y-α′-sialon is produced when Y_2O_3 and AlN in a mole ratio of 1:9 are added to Si_3N_4. It was reported that only Y-α′-sialon or both Y-α′-sialon and β-Si_3N_4 were obtained by sintering the mixtures of Si_3N_4, Y_2O_3 and AlN powders [2]. On the other hand, we have reported that Y-α′-sialon and β′-sialon are formed when the amount of Y_2O_3 and AlN added to Si_3N_4 is small, and moreover, that the lattice constant of the Y-α′-sialon increases with increasing amount of Y_2O_3 and AlN, while that of the β′-sialon is almost constant [3].

Although extensive studies have been conducted on the processing, phase diagram and mechanical properties of α′-sialon [1–7], very limited data have been reported on thermal expansion of α′-sialon [1–8]. In this study, the thermal expansion coefficient of Y-α′-sialon with a solubility lower than $x = 0.3$ and which coexists with β′-sialon has been determined by the high-temperature X-ray diffraction technique.

2. Experimental procedure

Six kinds of powder mixtures containing different total amounts of additives, Y_2O_3 and AlN, were prepared. For all the powder mixtures, the mole ratio of Y_2O_3 to AlN was kept at 1:9 as shown in Table I. The powder mixtures were hot-pressed using a graphite die with BN coating in a nitrogen atmosphere at 1850 °C under a pressure of 20 MPa for 1 h.

TABLE I Nominal compositions of powder mixtures and the content of Y-α′-sialon determined by X-ray analysis

	Si_3N_4 (mol %)	Y_2O_3 (mol %)	AlN (mol %)	x^a	α′ (vol %)
1	89.0	1.1	9.9	0.10	11
2	85.0	1.5	13.5	0.14	24
3	77.0	2.3	20.7	0.22	55
4	74.0	2.6	23.4	0.26	69
5	67.0	3.3	29.7	0.36	100
6	50.0	5.0	45.0	0.62	100

[a] x in $Y_x(Si, Al)_{12}(O, N)_{16}$.

Specimens of 15 mm × 20 mm × 0.4 mm were cut out from the hot-pressed discs to determine the thermal expansion coefficient by the high-temperature X-ray diffraction technique. The specimens were horizontally set in the centre of a high-temperature X-ray diffractometer. Lattice constants at various temperatures were obtained from the X-ray data measured up to 1000 °C in an ambient atmosphere, and the thermal expansion coefficient was calculated from the dependence of the lattice constant on temperature. Because plate type specimens instead of powder were used in this study, the internal standard could not be used. The method of measuring the thermal expansion coefficient of α-Si_3N_4 and the values obtained are the same as those obtained by Henderson and Taylor [9]. Therefore, errors due to geometrical change during heating were found to be very small.

The thermal expansion coefficients were also measured by a differential dilatometer using a silica bar as a standard from room temperature to 1000 °C at a heating rate of 5 °C min^{-1} in an ambient atmosphere. The specimen size was 3 mm × 4 mm × 40 mm. X-ray diffraction analysis revealed that β′-sialon grains were oriented perpendicular to the hot-pressing direction. However, the effect of this texture on the thermal expansion coefficient measured by a differential dilatometer was ignored, because the thermal expansion coefficients of the *a*- and *c*-axes of β′-sialon

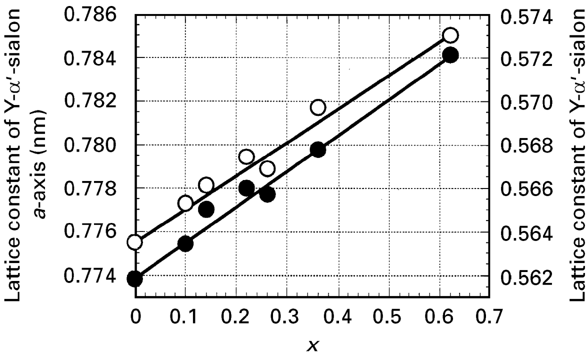

Figure 1 The relation between lattice constants of Y-α′-sialon and *x*. (○) *a*-axis, (●) *c*-axis.

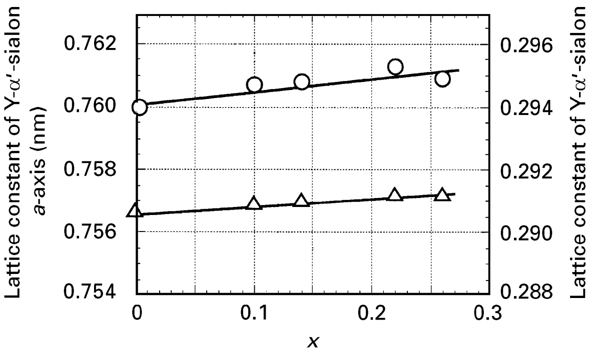

Figure 2 The relation between lattice constant of β′-sialon and *x*. (○) *a*-axis, (△) *c*-axis.

determined by the X-ray diffraction method were nearly the same, as described later.

3. Results and discussion

3.1. Dependence of lattice constant on the amount of Y_2O_3 and AlN

The relations between the amount of Y_2O_3 and AlN, namely *x* and lattice constants of the *a*- and *c*-axes for Y-α′-sialon and β′-sialon of all specimens at room temperature are shown in Figs 1 and 2. With increasing *x*, the lattice constant of Y-α′-sialon increased from 0.775 nm to 0.785 nm on the *a*-axis and from 0.562 nm to 0.572 nm on the *c*-axis while that of β′-sialon only slightly increased. The abscissa in each figure represents the *x* value in the general formula, $Y_x(Si_{12-4.5x}, Al_{4.5x})(O_{1.5x}, N_{16-1.5x})$. The *x* values were calculated from the nominal compositions of the mixtures shown in Table I by Equation 2,

$$x = [8(100 - S)/(7S + 300)] \qquad (2)$$

where *S* is the mole concentration of Si_3N_4. In this calculation, all the Y_2O_3 and AlN are assumed to have dissolved into α-Si_3N_4 to form Y-α′-sialon in accordance with Equation 1. If this assumption is valid, the crystalline phase formed should be Y-α′-sialon and β-Si_3N_4 when the amount of Y_2O_3 and AlN is small [2, 4]. This assumption is invalid, however, because some Y_2O_3 and some AlN was consumed to form β′-sialon in the reaction

$$(2-0.5z)Si_3N_4 + zAlN + 0.5zSiO_2 = Si_{6-z}Al_zO_zN_{8-z} \qquad (3)$$

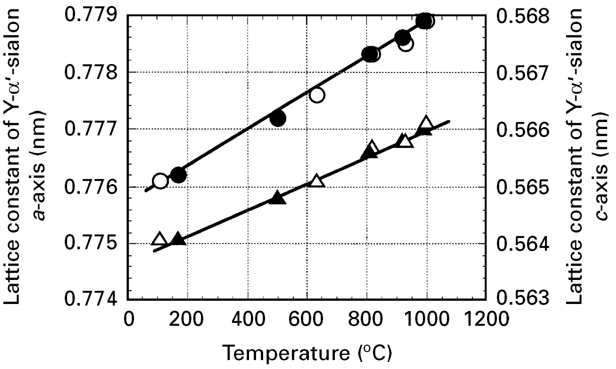

Figure 3 The relation between lattice constants of Y-α′-sialon and temperature: lattice constants of (○, ●) *a*- and (△, ▲) *c*-axis obtained in the (○, △) heating and (●, ▲) cooling processes.

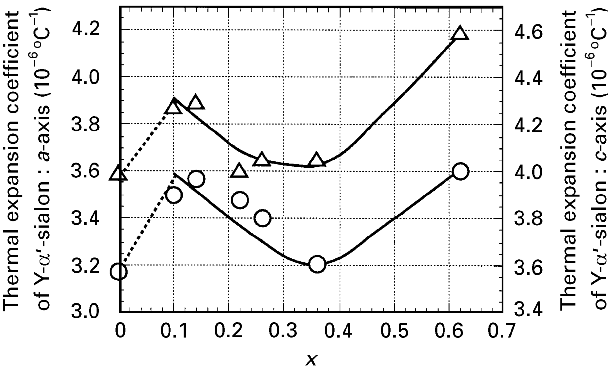

Figure 4 The dependence of thermal expansion coefficient of Y-α′-sialon on *x*: (△) *a*-axis, (○) *c*-axis.

where SiO_2 is an impurity usually contained in Si_3N_4 powder. For these reasons, the *x* values calculated from Equation 2 should be corrected by determining the compositions of the Y-α′-sialon fabricated. However, the determination seems very difficult or almost impossible, especially when the amount of Y_2O_3 and AlN is small, because the amount of Y-α′-sialon and the *x* value are also very small. Therefore, the *x* value calculated from the nominal compositions was used in this study.

3.2. Thermal expansion coefficient of Y-α′-sialon

The lattice constants of Y-α′-sialon were determined from the diffraction angles of the X-ray diffraction peaks obtained at various temperatures. The thermal expansion coefficient was calculated from the dependence of these lattice constants on temperature. The temperature dependence of the lattice constant of Y-α′-sialon in specimen 1 is shown in Fig. 3 as an example. The lattice constants of both the axes increased linearly with increasing temperature. The thermal expansion coefficients of the *a*- and *c*-axes of specimen 1 were calculated to be 3.87×10^{-6} and $3.90 \times 10^{-6}\,°C^{-1}$, respectively. The thermal expansion coefficients of Y-α′-sialon in all the specimens were thus determined and are summarized in Fig. 4. As shown in this figure, the thermal expansion coefficient of Y-α′-sialon discontinuously increased with increasing *x* in the region of $0 < x < 0.1$, decreased in the region of

TABLE II Thermal expansion coefficient of α-Si_3N_4 determined by the X-ray diffraction method

Thermal expansion coefficient $(10^{-6}\,^{\circ}C)^{-1}$ *a*-axis	*c*-axis	Reference
3.61	3.70	[9]
2.82	3.12	[10]
3.60	3.60	This work

$0.1 < x < 0.3$, and increased again in the region of $0.3 \leqslant x$.

The thermal expansion coefficients of α-Si_3N_4 obtained in three studies are compared in Table II. The coefficient obtained in this study is nearly equal to that obtained by Henderson and Taylor [9], who used the α-Si_3N_4 powder produced by nitridation of silicon, and is much higher than that obtained by Niihara and Hirai [10], who used the Si_3N_4 powder produced by the chemical vapour deposition process. The difference in these values may come from the difference in the amount of impurity in α-Si_3N_4 powders. In other words, the amount of impurities, such as metal cation or oxygen in the Si_3N_4 powder used by Niihara and Hirai is probably much smaller than those used by the present authors and Henderson and Taylor.

As shown in Fig. 4, the thermal expansion coefficient of Y-α'-sialon was larger than that of α-Si_3N_4. When Y_2O_3 and AlN are used, Y-α'-sialon is derived from α-$Si_{12}N_{16}$ by the partial replacement of Si^{4+} with Al^{3+} and N^{3-} with O^{2-}, and valency compensation is affected by Y^{3+} cations occupying the interstices of the (Si, Al)–(O, N) network [1]. This means that Si–N bonds are replaced by Al–N and Al–O bonds in the structure and lattice constants should increase, unless the modifying cation affects the structure. Therefore, the fact that the thermal expansion coefficient of Y-α'-sialon is larger than that of α-Si_3N_4 suggests that the intrinsic thermal expansion coefficients of the Al–N and the Al–O bonds are larger than that of the Si–N bond.

The dependence of the thermal expansion coefficient of Y-α'-sialon on x is not yet clearly understood. Yamai and Ota [8] have measured the thermal expansion coefficients of many kinds of α'-sialon such as Y-, Ca-, Li-, Sm- and Nd-α'-sialon to clarify the relation between the thermal expansion coefficient and the lattice constant. The thermal expansion coefficient of the *a*-axis was found to increase with increasing lattice constant of the *a*-axis, whereas the coefficient of the *c*-axis was found to decrease slightly at first and then increase. It is considered that this initial decrease results from the avoidance of structural collapse in α'-sialon by the incorporation of modifying cations, because the collapse in α'-sialon would easily vary with the kind of modifying cation and the thermal expansion coefficient may be somewhat influenced by the structural collapse.

The lattice constants of *a*- and *c*-axes are proportional to x, as shown in Fig. 1, and the thermal expansion coefficients of the *a*- and *c*-axes of Y-α'-sialon decrease with increasing lattice constant and then increase, as shown in Fig. 4. These results suggest that the structural collapse in α'-sialon is influenced not only by the kind of modifying cation, but also by its concentration.

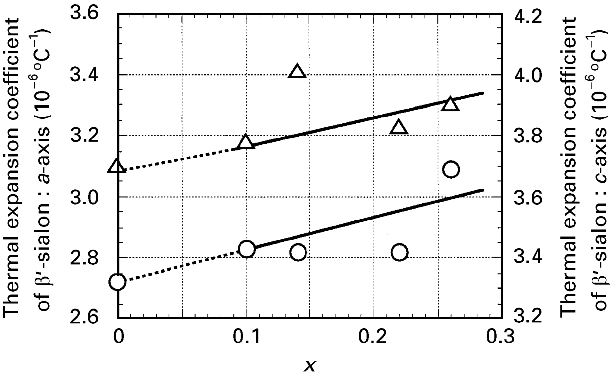

Figure 5 The dependence of thermal expansion coefficient of β'-sialon on x: (△) *a*-axis, (○) *c*-axis.

Izumi *et al.* [6] have conducted a structural analysis of Y-α'-sialon in the region of $0.3 \leqslant x$ by using rietveld refinement. However, the structure in the region of $0.3 > x$ should be also analysed in order to check whether the structures of Y-α'-sialon in the two regions are different, which would explain the dependence of the thermal expansion coefficient on x.

3.3. Thermal expansion coefficient of β′-sialon

The thermal expansion coefficient of β'-sialon increased with increasing x as shown in Fig. 5. Because the z value, namely the lattice constants, increased with increasing x as shown in Fig. 2, it can be said that the thermal expansion coefficient increases with increasing lattice constants. Moreover, the thermal expansion coefficient of the *c*-axis was larger than that of the *a*-axis. These results agree well with those obtained by Yamai and Ota [8]. It is also considered that (Si, Al)(O, N) tetrahedra in β'-sialon are greatly elongated in the *c*-axis direction compared with SiN_4 tetrahedra in β'-sialon, and that the larger Al–N bond is preferentially distributed in the *c*-axis direction. These facts are assumed to support the fact that the thermal expansion coefficient of the *c*-axis is larger than that of the *a*-axis.

3.4. Thermal expansion coefficient determined by differential dilatometer

Fig. 6 shows the thermal expansion coefficient determined by a differential dilatometer. The thermal expansion coefficient of the bulk body increases with increasing x, that is, the amount of Y_2O_3 and AlN. The thermal expansion coefficient of Y-α'-sialon with $x = 0.6$ determined using a dilatometer was $3.7 \times 10^{-6}\,^{\circ}C^{-1}$ [11]. The result obtained in this study is somewhat larger than that obtained by Mitomo *et al.* [11].

Fig. 6 also shows the thermal expansion coefficient, $\alpha(t)$, calculated from

$$\alpha(t) = V(\alpha)[\alpha(\alpha_a) + V(\beta)]\alpha(\beta_a) \qquad (4)$$

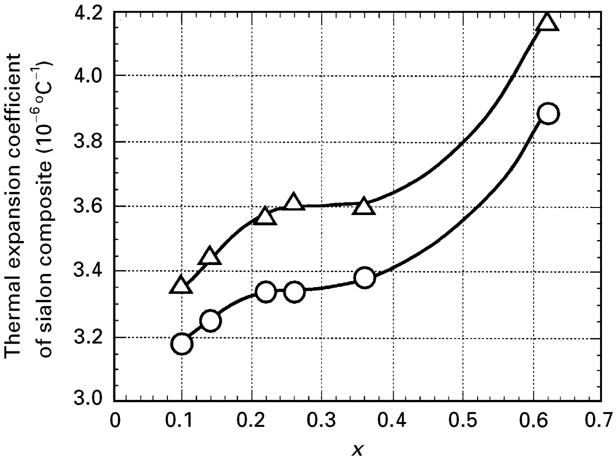

Figure 6 The dependence of thermal expansion coefficient determined by (○) differential dilatometry and (△) XRD, calculation of Equation 4 on x.

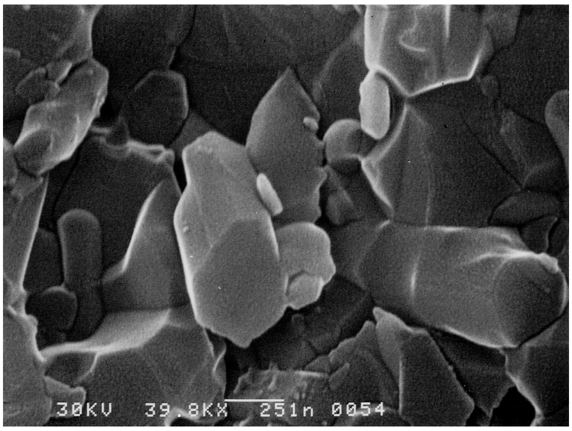

Figure 7 The fracture surface of sialon composite composed of Y-α′-sialon and β′-sialon with $x = 0.1$.

where $V(\alpha)$ and $V(\beta)$ are the volume fractions determined by the X-ray diffraction method listed in Table I, and $\alpha(\alpha_a)$ and $\alpha(\beta_a)$ are the thermal expansion coefficients of the a-axis, both of Y-α′-sialon and β′-sialon. $\alpha(t)$ is somewhat larger than the thermal expansion coefficient determined by the dilatometer, but their dependence on x is nearly the same.

3.5. Properties of sialon composite composed of Y-α′-sialon and β′-sialon

Sialon composites composed of Y-α′-sialon and β′-sialon have some interesting and excellent properties. For example, Ukyo and Wada [12, 13] have shown that the hot-pressed sialon composite composed of about 10 vol % Y-α′-sialon and 90 vol % β′-sialon has extremely high strength, 1.3 GPa at room temperature and 1.0 GPa at 1400 °C, and a fracture toughness of about 7.0 MPa m$^{1/2}$, in spite of its fine grains (~ 1.0 μm). The x value of this material is about 0.1. Fig. 7 shows the fracture surface of this material. Intergranular fracture and pull-out of small prismatic grains (β′-sialon) are observed on the fracture surface, which are considered to cause high fracture toughness. Fig. 8 shows the difference in the thermal expansion coefficients of the a-axis of Y-α′-sialon and β′-sialon. The difference became maximum at $x = 0.1$. The difference in the thermal expansion coefficients may also cause the grain-boundary stress. Therefore, it is considered that the difference in the thermal expansion coefficients leads to high fracture toughness as well as large aspect ratio of β′-sialon.

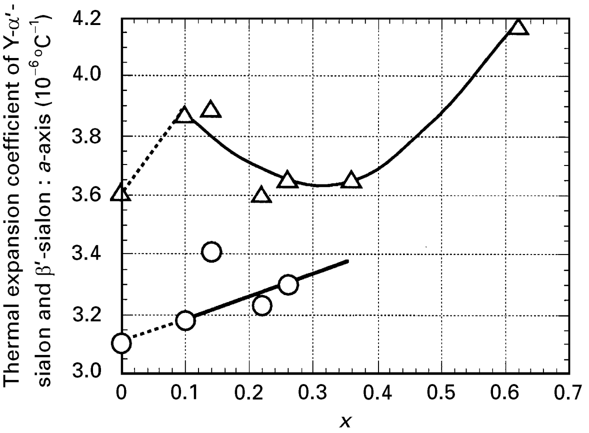

Figure 8 The dependence of thermal expansion coefficient of (△) Y-α′-sialon and (○) β′-sialon on x.

4. Conclusions

The thermal expansion coefficients of Y-α′-sialon with various solubilities were measured by the high-temperature X-ray method. The results obtained are as follows.

1. The thermal expansion coefficient of Y-α′-sialon discontinuously increased with increasing x in the region of $0 < x < 0.1$, decreased in the region of $0.1 < x < 0.3$, and then increased again in the region $0.3 < x$.
2. The thermal expansion coefficient of β′-sialon increased with increasing lattice constant, or z value in $Si_{6-z}Al_zO_zN_{8-z}$.
3. The thermal expansion coefficient determined by a differential dilatometer increased with x.
4. The difference in the thermal expansion coefficients between Y-α′-sialon and β′-sialon became maximum at $x = 0.1$. The x value at which sialon composite, composed of Y-α′-sialon and β′-sialon, has high strength and high fracture toughness, was also $x = 0.1$.

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