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The microstructure of hot-pressed sialon polytypes

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The sialons – phases in the Si–Al–O–N and related systems – form the basis of a new group of engineering ceramics, the successful application of which depends on their chemical stability and resistance to microstructural changes at elevated temperature. In the Si–Al–O–N system a new series of polytypes exists in which the structure is determined by the metal : non-metal atom ratio. The polytypes coexist in extensive two-phase regions which are important in determining the way that microstructure and properties develop during the fabrication and subsequent use of the material. In an electron microscopic investigation of some sialon polytypes, diffraction contrast and direct lattice imaging are used to follow changes in microstructure during hot-pressing, and to determine the nature of lattice imperfections and stacking arrangements.

1. Introduction

1.1. Silicon nitride and the sialons

The unique properties of silicon nitride – high strength, oxidation and corrosion resistance, thermal stability and resistance to thermal shock – make it a favoured material for ceramic gas turbine components and other high performance applications. However, because it is a covalent solid its self-diffusivity is low and so it is not easily densified by the high temperature firing used for conventional oxide ceramics. In attempts to overcome this difficulty the concept of "ceramic alloying" was developed concurrently in Japan [1] and England [2] and it was shown that nitrogen in silicon nitride could be widely replaced by oxygen if, at the same time, silicon was replaced by aluminium. The resulting β'-sialon is more stable than silicon nitride [3], has the same combination of desirable properties, but can be densified by hot-pressing or pressureless sintering (see Jack [4]). By incorporating a third metal, the five component M–Si–Al–O–N systems (M = Li, Mg, Y, Ca, Ce, Zr, Sc) show phases with a wide variety of structure types [4], and it is now apparent that the sialons are essentially silicates and alumino-silicates in which oxygen is partly or completely replaced by nitrogen. Silicon nitride is thus only the first of a new field of materials that is potentially as wide as that of the mineral silicates.

The relationships between Si–Al–O–N condensed phases are represented by a behaviour diagram in which, as in a reciprocal salt system, concentrations are expressed in equivalents (Fig. 1). Thus, any point in the square diagram Si_3N_4–Al_4O_6–Al_4N_4–Si_3O_6 represents a combination of 12+ and 12− valencies, where the components adopt their usual valency states, that is Si^{4+}, Al^{3+}, N^{3-} and O^{2-}.

1.2. Sialon polytypes

Sialon compositions between β' and AlN form six phases (see Fig. 1) which have structures based on the AlN wurtzite-type. These phases are members of a new series of polytypes in which the structure is determined by the metal : non-metal atom ratio M : X. The polytypes have compositions M_mX_{m+1} where m is an integer 4 to 9, and the structures are described by the Ramsdell symbols 8H, 15R, 12H, 21R, 27R and 2H[δ]. As shown in Table I there are n double layers MX along the c-dimension of the hexagonal (H) or rhombohedral (R) unit cell where n is the Ramsdell numeral and $n_H = 2m$, $n_R = 3m$. Hexagonal polytypes thus contain two, and rhombohedral polytypes contain three symmetry-related

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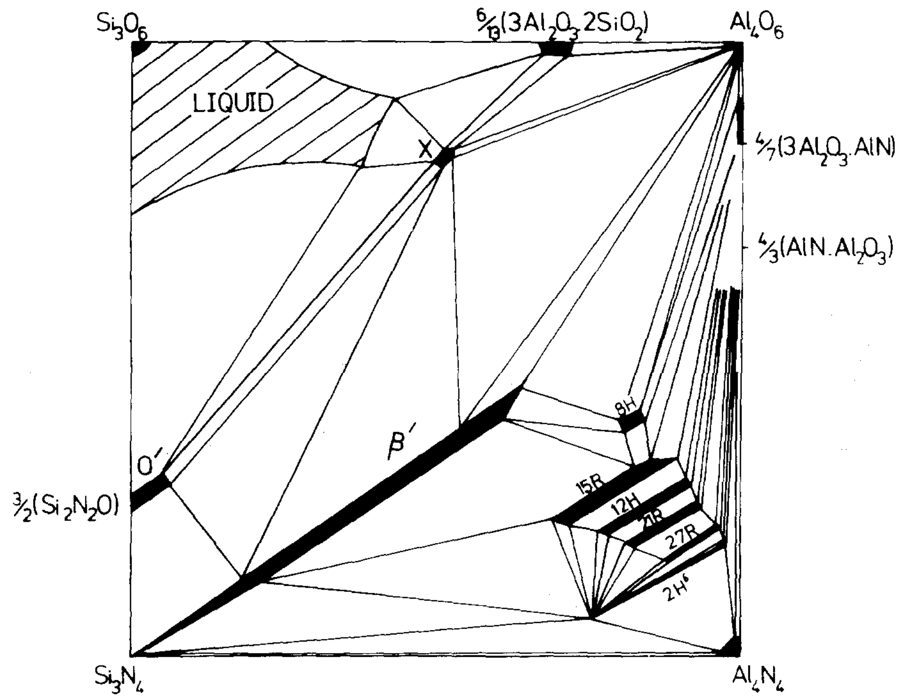

Figure 1 The Si–Al–O–N system (1750° C).

blocks, each of *m* layers, per unit cell. One layer in each block of *m* layers contains an extra non-metal atom X which thus becomes an MX_2 layer. Occupation of all the tetrahedral sites in a hexagonal close packed (h c p) array of metal atoms to give a composition MX_2 requires an impossibly short distance between non-metal atoms which is avoided by a local change in stacking from h c p ABAB . . . to f c c ABCAB . . . Each polytype then contains a stacking fault and an MX_2 layer in each block of structure. Examples of the simplified and idealized stacking arrangements in 15R and 12H are shown schematically by Fig. 2. The structures were determined at Newcastle by Thompson [5] whose recent refinement [6] shows that some metal atoms in "MX_2" regions statistically occupy more than one site and that AlO_6 octahedra occur midway between successive "MX_2" regions.

In the Si–Al–O–N system (Fig. 1) the pure phases show extensive ranges of homogeneity along lines of constant M:X ratio but are extremely limited in other directions. Thus, there are extensive two-phase regions which are important in determining the way that microstructure and properties develop during the high-temperature synthesis and subsequent use of the material. Successful application as an engineering ceramic depends on chemical and microstructural stability at elevated temperatures. In the present work, transmission electron microscopy is used to study sialon polytypes produced by hot-pressing. Conventional diffraction contrast images reveal stacking faults and other imperfections in solids and can be used to obtain quantitative information of the distribution of disorder. To determine the exact nature of the disorder, however, it is necessary to examine crystals by direct lattice imaging.

2. Experimental

Samples of 8H + 15R and 12H + 15R polytypes were prepared by hot-pressing powder mixtures of AlN, Al_2O_3 and Si_3N_4 at temperatures in the range 1600 to 1750° C. The powder mixture is wet-milled in ethanol, dried, and a pellet prepared by cold isostatic pressing. This is then hot-pressed pseudo-isostatically using boron nitride as the powder vehicle.

TABLE I Si–Al–O–N "AlN" polytypes

M/X	Type	*a* (Å)	*c* (Å)	*c*/*n* (Å)
4/5	8H	2.988	23.02	2.88
5/6	15R	3.010	41.81	2.79
6/7	12H	3.029	32.91	2.74
7/8	21R	3.048	57.19	2.72
9/10	27R	3.059	71.98	2.67
δ	$2H^{\delta}$	3.079	~5.30	2.65
1/1	2H	3.114	4.986	2.49

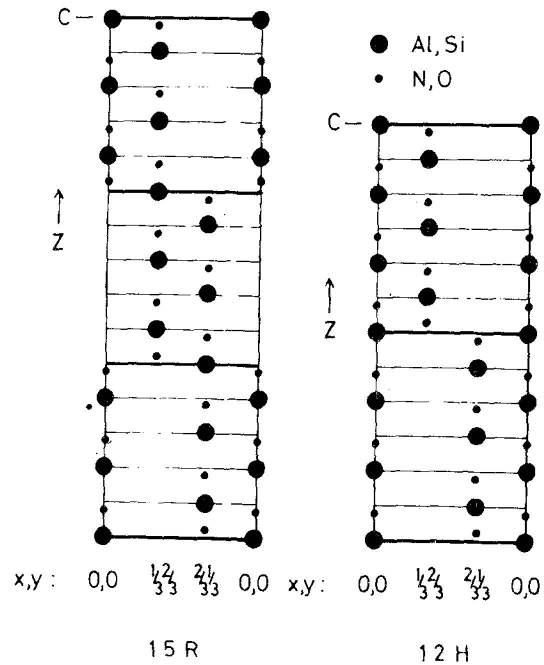

Figure 2 Idealized stacking arrangements in 15R and 12H Si–Al–O–N polytypes.

To examine grain boundaries and other polycrystalline features, foils for transmission electron microscopy are prepared by grinding on diamond paste to form a thin slice which is then thinned to perforation in a beam of argon ions. The perforated foil is coated with carbon for examination in the electron microscope. Single crystal fragments are prepared by immersing the sample in liquid nitrogen and then crushing in an agate mortar. The powder is dispersed in chloroform and a single drop placed on a perforated carbon support grid and dried. Specimens were examined in Philips EM300 and JEOL 100B microscopes using goniometer stages at direct magnifications up to x 800 000.

Bright-field direct lattice images were obtained from symmetrical axially aligned systematic rows of {0 0 1} reflections. Objective astigmatism was fully corrected for and a through-focal series of micrographs recorded at successive increments of defocus to facilitate selection of the optimum image.

3. Results and discussion

Polytypes prepared by hot-pressing consist of thin elongated grains aligned perpendicular to the applied pressure and with the crystal *c*-axis perpendicular to the long axis of the grains; see Fig. 3. A typical disordered microstructure in a specimen of 8H + 15R composition imaged by diffraction contrast is shown in Fig. 4. Both grains, separated by a high-angle grain boundary, show extensive disorder which is also evident from the inset diffraction pattern. Examination by lattice imaging shows that the disorder is of two types. In specimens prepared by heating for short times at low temperature, extensive intergrowth of polytypes occurs. During the early stages of reaction a number of polytypes form in addition to the equilibrium phases. An example is shown in Fig. 5 in which a variety of fringe widths occurs in a sample of equilibrium composition 12H + 15R. The fringes correspond to individual blocks of structure. From left to right in Fig. 5 the following sequence appears:

(1) a single block of width corresponding to that calculated for one block of 33R polytype. Because this polytype has not been observed by X-ray diffraction the block probably has a composition between $2H^{\delta}$ and AlN;

Figure 3 Microstructure of hot-pressed 8H + 15R Si–Al–O–N polytype.

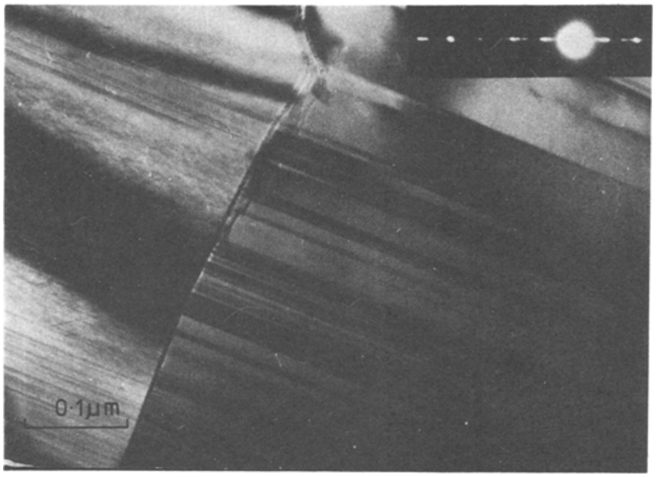

Figure 4 Disordered sample of (8H + 15R) hot-pressed at 1750° C – diffraction contrast image.

(2) a single block of 27R;
(3) seven blocks of 21R; and
(4) a large area of 12H polytype.

Since polytypes of high Ramsdell numeral are rich in Al and N, the fringe pattern corresponds with a composition gradient from AlN at the left of Fig. 5 becoming increasingly rich in Si and O toward the right. Equilibrium is therefore approached from AlN-rich compositions by diffusion of Si and O into AlN crystals, but has clearly not been attained after 15 min at 1650° C. With increased time or at a higher hot-pressing temperature, fewer intergrowths occur and consist of the equilibrium phases only. An example is shown in Fig. 6.

A second type of disorder occurs in specimens heated for short times at 1700° C and results in diffraction streaking. The streaks arise from planar faults in an extensive area of perfect crystal and in the example shown in Fig. 7, the single wide fringe spacing at the fault is equivalent to one additional MX layer in a single block of 15R structure. The five-layer blocks of 15R are therefore interrupted by a single six-layer block, that is, one block of 12H polytype. Confirmation of this stacking sequence is obtained in high resolution images of the 2.8 Å MX double layer spacing. Four weak fringes can be seen within the strong white fringes in Fig. 8, the latter corresponding to the fringes shown in the previous micrographs (Figs. 5 to 7). The five-layer blocks are interrupted, however, at A in Fig. 8 by single blocks of six layers which are faults similar to that shown in Fig. 7.

Samples hot-pressed for one hour at 1750° C consist of elongated grains of perfect polytypes of equilibrium composition. Fig. 9 is an example of 15R in a 12H + 15R polytype composition. The unit cell c-dimension of 41.8 Å determined by X-ray diffraction is seen to consist of 3 blocks each of five layers with a layer spacing of 2.78 Å (see Table I). Thus, there is direct visual confirmation of the structure proposed by Thompson [5] and shown in Fig. 2. Similar images of 15R in Be–Si–Al–O–N polytypes $M_{m+1}X_m$ which are antitypes of the Si–Al–O–N series have been reported by Clarke *et al.* [7].

4. Conclusions

The microstructure of two-phase mixtures of sialon polytypes consists of elongated grains aligned perpendicular to the hot-pressing direction and with the crystal c-axis perpendicular to the long axis of the grains. Samples prepared by hot-pressing at

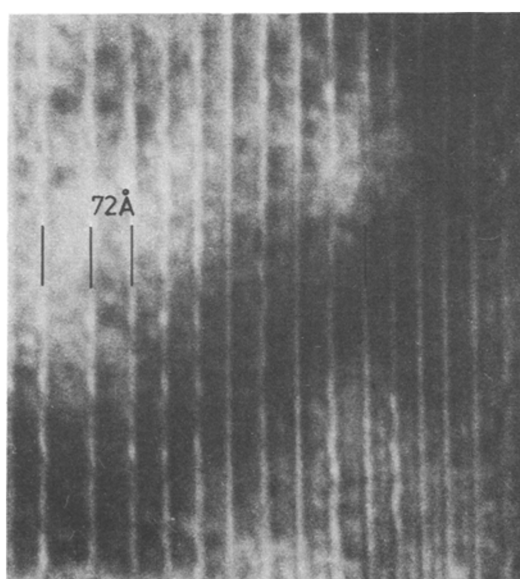

Figure 5 12H + 15R hot-pressed for 15 min at 1650° C.

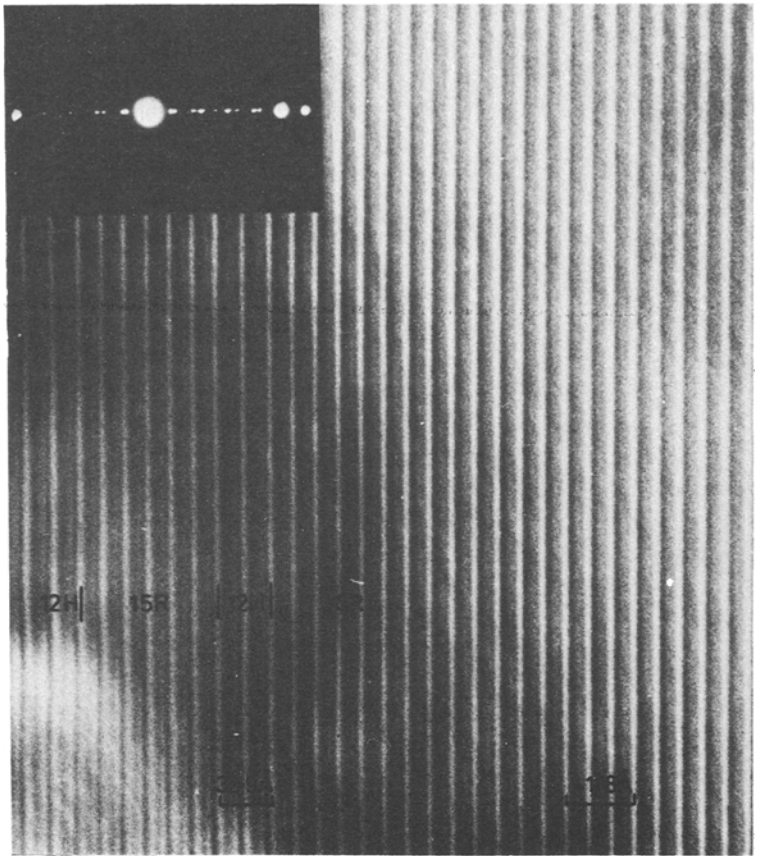

Figure 6 12H + 15R hot-pressed for 15 min at 1750° C.

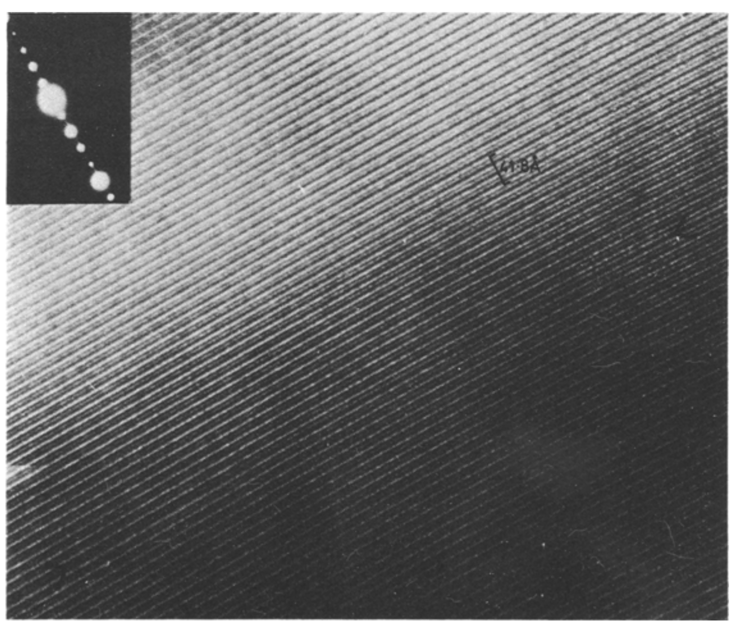

Figure 7 12H + 15R hot-pressed at 1750° C – 15R polytype crystal.

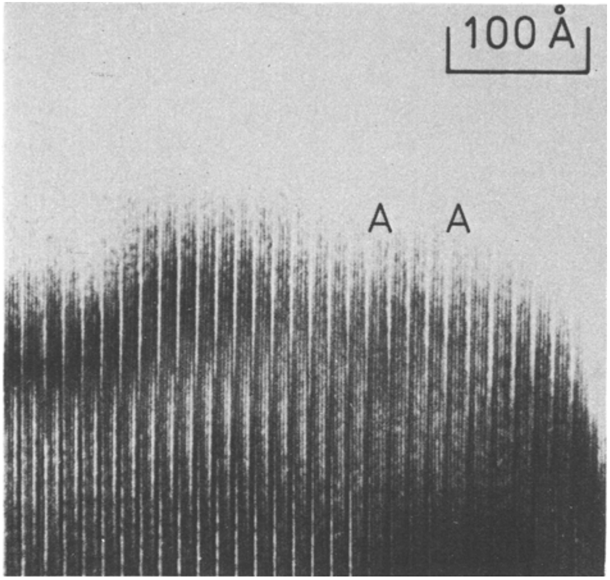

Figure 8 High resolution lattice image of a faulted 15R crystal.

1600° C for 15 min (low temperature and short time) are heavily disordered and the amount of disorder decreases as the fabrication temperature is increased. After one hour at 1750° C, perfect polytype crystals of equilibrium composition are formed which are separated by high-angle grain boundaries.

Direct lattice imaging shows that intergrowth of polytypes and stacking faults occur at low hot-pressing temperature and that chemical equilibuium is approached by diffusion of silicon and oxygen into AlN to form polytypes of high Ramsdell numeral which homogenize at higher temperature and after longer times.

Direct lattice imaging and electron diffraction confirm the stacking sequence of MX layers in sialon polytypes $M_m X_{m+1}$ previously determined by X-ray diffraction. The unit cell consists of n layers sub-divided into two or three blocks each of m layers, where n is the Ramsdell numeral of hexagonal (H) and rhombohedral (R) polytypes and where $n_H = 2m$, $n_R = 3m$. The individual layer spacing is 2.8 Å:

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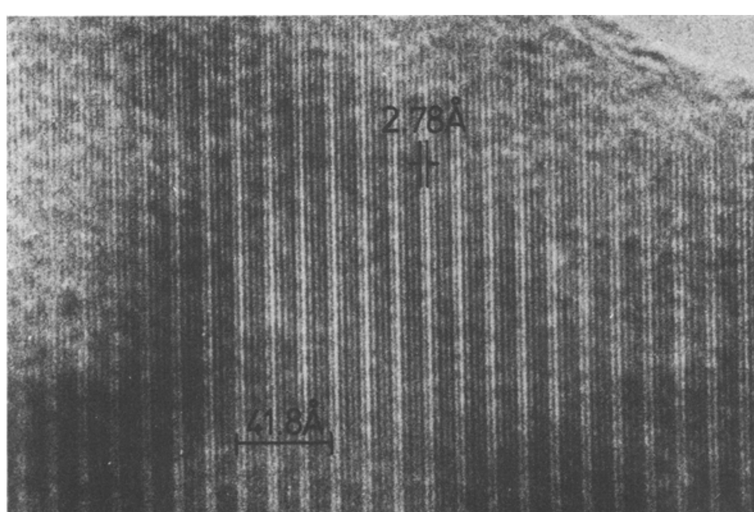

Figure 9 15R Si–Al–O–N polytype.

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