JOURNAL OF MATERIALS SCIENCE **26** (1991) 1585–1587

Nitrogen-containing aluminium titanate

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In the Ti–Al–O–N system a phase isostructural to aluminium titanate but with expanded unit cell dimensions was observed. It was stable between 1400 and 1700 °C and has unit cell dimensions of $a = 0.3719$ nm, $b = 0.9703$ nm and $c = 0.9869$ nm with a composition of $Ti^{4+}_{1.00}Al^{3+}_{0.54}Ti^{3+}_{1.46}N^{3-}_{0.28}O^{2-}_{4.58}\square_{0.14}$. Several samples were prepared by reaction sintering mixtures of TiN, Al_2O_3 and AlN powders at 1400 to 1470 °C for 4 h in a nitrogen atmosphere to maximize this phase. One specific advantage of the nitrogen-containing aluminium titanate over aluminium titanate is that the former is unchanged at 1150 °C in a nitrogen atmosphere whereas the latter decomposes. In the Al_2O_3–TiO_2 oxide system Al_2TiO_5 solid solution extends to approximately $Al_{0.75}Ti_{2.25}O_5$ at 1470 °C under the mildly reducing conditions of a graphite furnace. The unit cell volume increases linearly with the increasing replacement of Al^{3+} by Ti^{3+}.

1. Introduction

In the investigation of the Ti–Al–O–N system a nitrogen-containing aluminium titanate of composition $Ti_{1.81}Al_{1.03}N_{0.34}O_{4.66}$ (denoted by NAT) prepared from AlN, Al_2O_3 and TiO_2 was observed between 1400 to 1700 °C [1]. A previous attempt has been made to produce a Ti–Al–O–N phase by reacting a mixture of $2TiO_2$–AlN at 1400 °C [2]. The phases observed were TiN, Al_2O_3, and a pseudobrookite $(Al,Ti)_2TiO_5$ phase but no evidence was presented for the presence of any nitrogen in the latter. A similar pseudobrookite phase was shown to be a solid solution between Ti_3O_5 and aluminium titanate (denoted by AT) by Asbrink and Magneli in argon [3] and by Goldberg in Ar–H_2 atmospheres [4]. Goldberg showed the existence of an orthorhombic structure for $0.5 \leqslant x \leqslant 2.0$ in the formula $(Al_xTi_{2-x})TiO_5$ (denoted by AT′) and a related monoclinic structure for $x < 0.5$.

The aim of this work was to investigate in detail the NAT phase and study the variation of the unit cell dimensions with different levels of titanium and nitrogen substitution. To elucidate interpretation compositions between TiO_2 and Al_2TiO_5 were also prepared. In the work presented here compositions made with AlN, Al_2O_3 and TiO_2 have been reacted at 1400 to 1720 °C in nitrogen.

2. Experimental

The compositions shown in Fig. 1 were prepared using AlN, TiO_2 and Al_2O_3 powders, except for composition I which was made from TiN–TiO_2–AlN. The representation of the Ti–Al–O–N system by a square composition diagram has been discussed [1]. The mixtures were hand mixed in ethanol in an agate pestle and mortar, dried and compacted into pellets. They were fired in a carbon resistance furnace in a graphite crucible on a bed of boron nitride in a dynamic nitrogen atmosphere. Sintering was carried out for 4 h at reaction temperatures; details of the powders, mixing and firing are given elsewhere [1]. Firings in air were carried out in an electric muffle furnace in a platinum dish.

The fired pellets were ground to −150 μm and analysed by X-ray diffraction (XRD) using a Philips PW1700 Series Automated Diffractometer with Co Kα radiation and Philips software. The thermogravimetric analysis (TGA) was carried out in nitrogen at 8 °C min^{-1} up to 1500 °C (analyst: Dr I. W. M. Brown, Swedish Ceramic Institute, Sweden) and in air at 10 °C min^{-1} up to 1150 °C (analyst: Dr N. Tapp, Chemistry Division, DSIR). The polished sections of fired samples were analysed for aluminium and titanium by energy dispersive X-ray analysis and the nitrogen analysis was carried out on a powdered sample by the Kjeldahl method (analyst: Mr G. C. Murray, Coal Research Association Inc., New Zealand).

3. Results and discussion

3.1. TiO_2–Al_2O_3 system

Along the $2Al_2O_3$–$3TiO_2$ join (Fig. 1) compositions were reacted at 1470 °C for 4 h XRD analysis of sample K showed the major phase as AT as expected from its starting composition, while samples with increasing TiO_2 content produced the substituted AT′ phase. Traces of corundum were also observed in the XRD patterns of these samples. The composition A was also reacted at 1550 °C with a similar result to the lower temperature firing. Samples P and N initially showed two distinct AT′ compositions which merged on heating for a further 4 h. There was a gradual increase of unit cell dimensions in the AT phase with increasing Ti^{3+} substitution, as shown by an increase in cell volume in Fig. 2. The b and c dimensions

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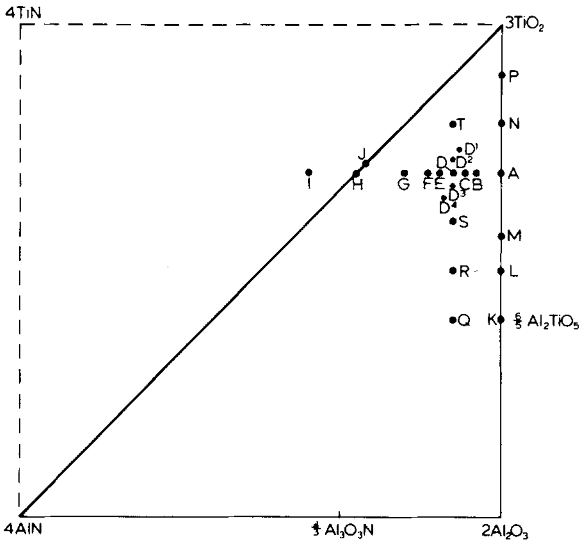

Figure 1 The square representation of the Ti–Al–O–N system, showing the compositions prepared in this study.

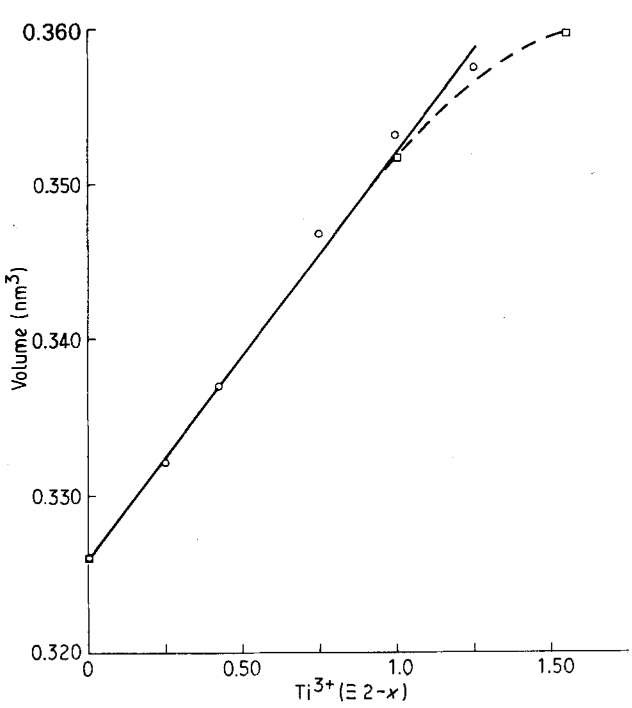

Figure 2 Variation of unit-cell volume with Ti^{3+} content in $Ti^4Al_x^{3+}Ti_{2-x}^{3+}O_5^{2-}$ (□ Goldberg, ○ this work).

increased more than *a* showing some degree of anisotropy. Goldberg [4] suggested that this increase was due to Ti^{3+} substituting into Al^{3+} at octahedral sites, with and Ti^{4+} remaining in the same octahedral sites in the unit cell. The increase of unit cell volume is as expected because the octahedral ionic radius of Ti^{3+} (= 0.081 nm) is larger than that of Al^{3+} (= 0.053 nm) [5]. Goldberg's results coincide with this work up to $Ti^{3+} = 0.088$ and deviate slightly above that (Fig. 2). When TiO_2 alone was heated the product was an equal mixture of Ti_7O_{13} and Ti_8O_{15}, showing that the atmosphere is only mildly reducing; however in more reducing conditions such as H_2–Ar atmospheres Ti_3O_5 has been observed [4].

3.2. TiO_2–Al_2O_3–AlN system

Moving from composition A to I (Fig. 1) the Al–Ti ratio remains constant while the amount of nitrogen is increased. These compositions were reacted at 1470 °C for 4 h and their XRD analyses are listed in Table I with the ratios of relative intensities of corundum 113–NAT 023 and of TiN 200–NAT 023. The composition D had a very thin surface coating of TiN, on removing this TiN disappeared from the XRD pattern. The unit cell volumes of the orthorhombic phase in compositions A to I are also listed in Table I. There was a slight increase in the cell volume moving from A to C and a larger increase from A to D. Because the Al–Ti ratio is constant, this increase is due to the replacement of oxygen by nitrogen in the unit cell to form a nitrogen-containing aluminium titantate (NAT). Moving from D to I the unit cell volume of this NAT phase remains constant, while the amounts of both corundum and TiN increased. The composition D had the strongest peaks of NAT, although it had about 10% corundum as a second phase. The composition J ($2TiO_2$/1AlN) gave a result similar to that reported by Mocellin and Bayer [3], behaving similar to composition I. The unit cell volumes of compositions Q to T were also same as that of D. The amount of corundum increased from S to Q, reflecting the amount of alumina in the starting composition and was the major phase of composition Q.

Most of the compositions when fired at 1550 °C for 4 h gave results similar to the 1470 °C firings, but in some cases the unit cell volume of NAT was slightly smaller. At 1720 °C NAT was not observed but only TiN and corundum; at this temperature TiO_2 reacts with AlN to form TiN and corundum.

3.3. Nitrogen-containing aluminium titanate

The starting composition D (Fig. 1), i.e. $Ti_{1.81}Al_{1.03}N_{0.34}O_{4.66}$ which could also be represented as $2.1TiO_2:0.4Al_3O_3N$ was selected for further study. To see whether there is any solid solubility in the direction of $3TiO_2$–4/3 Al_3O_3N, compositions D1 and D4 were reacted and the unit cell of the NAT phase measured. The resultant cell volumes were the same as that measured from composition D, indicating little or

TABLE I XRD Analysis of fired compositions in the Ti–Al–O–N system

Composition	Phase analysis	Unit cell volume, (nm^3)	I_C/I_A[a]	I_T/I_A[a]
A	AT'	0.3436	–	–
B	NAT ≫C	0.3439	0.13	–
C	NAT ≫C	0.3487	0.19	–
D	NAT ≫C	0.3562	0.17	–
E	NAT > C≫TiN	0.3563	0.63	0.12
F	NAT > C > TiN	0.3563	0.43	0.40
G	NAT, TiN, C	0.3565	0.39	0.65
H	TiN > NAT > C	0.3562	0.52	1.42
I	TiN > NAT > C	0.2562	0.70	2.74

[a] I_C = Relative intensity of corundum (C), 113.
I_T = Relative intensity of TiN, 200.
I_A = Relative intensity of NAT, 023.

no solid solubility. Similarly D2 and D3 also did not show a different cell volume to composition D. They all had corundum as a second phase—more in D3 and D4 than in D. They also had a thin surface coating of TiN similar to D.

The Al–Ti ratio (by EDX analysis) of the fired composition D combined with a separate nitrogen assay resulted in the formula $\mathrm{Ti}^{4+}_{1.00}\mathrm{Al}^{3+}_{0.54}\mathrm{Ti}^{3+}_{1.46}\mathrm{N}^{3-}_{0.28}\mathrm{O}^{2-}_{4.58}\square_{0.14}$ for the NAT phase. This was calculated on the basis of nitrogen substitution for oxygen in the formula $\mathrm{Ti}^{4+}\mathrm{Al}^{3+}_{x}\mathrm{Ti}^{3+}_{2-x}\mathrm{O}^{2-}_{5}$. The overall reaction for the formation of the NAT phase can be represented as $1.36\ [\mathrm{Ti}_{1.81}\mathrm{Al}_{1.03}\mathrm{N}_{0.34}\mathrm{O}_{4.66}] \rightarrow \mathrm{Ti}_{2.46}\mathrm{Al}_{0.54}\mathrm{N}_{0.28}\mathrm{O}_{4.58}\square_{0.14} + 0.43\ \mathrm{Al_2O_3} + 0.33\ \mathrm{O} + 0.18\ \mathrm{N}$. This represents a weight loss of 3.0%, in agreement with the weight loss of 3% measured between 800 to 1400 °C by TGA. Mocellin and Bayer [3] showed by TGA that heating $\mathrm{TiO_2}$–AlN mixtures from ambient to 1400 °C resulted in both oxygen and nitrogen being lost.

The lattice spacings of fired composition D are listed in Table II, which shows the strongest intensity to arise from the 023 peak whereas in AT the 110 is the strongest reflection [6]. This is more likely due to orientation effects rather than due to nitrogen substitution because different patterns of both NAT and AT′ had either the 023 or the 110 as the major peak apparently at random. The diffraction pattern of D shows it to be of similar structure to that of AT. The unit cell volume of composition D after heating at 1550 °C for 4 h was 0.3551 nm^3, a value slightly smaller than that at 1470 °C (Table II). This may be due to loss of some nitrogen.

TABLE II Lattice spacings of $\mathrm{Ti}^{4+}_{1.00}\mathrm{Al}^{3+}_{0.54}\mathrm{Ti}^{3+}_{1.46}\mathrm{N}^{3-}_{0.28}\mathrm{O}^{2-}_{4.58}\square_{0.14}$

Orthorhombic, *Cmcm*, $a = 0.3719$ nm, $b = 0.9703$ nm, $c = 0.9869$ nm, $V = 0.3562\ \mathrm{nm}^3$

h k l	d_{calc} (nm)	d_{obs} (nm)	I_{obs}
0 0 2	0.4935	0.4926	11
0 2 0	0.4852	0.4849	44
0 2 2	0.3473	0.3470	83
1 1 0	0.3460		
1 1 1	0.3276	0.3271	9
1 1 2	0.2840	0.2833	4
0 2 3	0.2723	0.2721	100
0 0 4	0.2467	0.2466	2
1 3 0	0.2441	0.2439	16
0 4 0	0.2426	0.2425	9
1 1 3	0.2388	0.2386[a]	18
0 2 4	0.2199	0.2198	21
0 4 2	0.2177	0.2175	36
0 4 3	0.1952	0.1951	33
2 0 0	0.1859	0.1860	18
0 2 5	0.1828	0.1827	15
1 3 4	0.1740	0.1741[a]	15
0 0 6	0.1645	0.1645	18
1 5 2	0.1625	0.1624	15
0 6 1	0.1596	0.1596	5
0 2 6	0.1558	0.1558	5
2 2 3	0.1536	0.1535	16
1 5 3	0.1525	0.1525	13

[a] Overlap with corundum.

3.3. Stability of nitrogen-containing aluminium titanate

When either AT or NAT (fired composition D) were heated in air at 1150 °C for 5 h, the resultant products were rutile and corundum. Under the same conditions, TGA showed a 5.1% weight gain for NAT which compares favourably with the theoretically expected weight gain of 4.9%. The same material when heated in nitrogen at 1150 °C for 5 h showed no change in weight (TGA) or in its XRD pattern. However, AT under similar conditions decomposed almost completely to rutile and corundum. This clearly shows NAT to be stable in a nitrogen atmosphere under conditions where AT is not. The Ti–N bond is more covalent than the Ti–O bond [7], reflected in the melting point of TiN (2950 °C) and TiO (1737 °C), therefore the former would be expected to be more stable.

Since crystalline nitrogen ceramics exhibit superior thermal and mechanical properties to equivalent oxide ceramics, it is reasonable to expect that this woud apply to nitrogen-containing aluminium titanate, therefore further explorations of physical and mechanical properties are being carried out.

4. Conclusions

Nitrogen containing aluminium titanate of orthorhombic structure isostructural with aluminium titanate can be formed above 1400 °C and is stable up to ≈ 1700 °C. Although it decomposes in air similarly to aluminium titanate at 1150 °C, it is stable in a nitrogen atmosphere for up to 5 h at this temperature; whereas aluminium titanate decomposes under these conditions. Further exploration of these materials is warranted for use as engineering ceramics.

Acknowledgements

Authors thank the following staff of the DSIR: K. A. Card for EDX analysis, I. W. M. Brown and N. Tapp for TGA.

References

1. D. S. PERERA, submitted to *Brit. Ceram. Soc. Trans. & J.* **89** (1990) 57.
2. A. MOCELLIN and G. BAYER, *J. Mater. Sci.* **20** (1985) 3697.
3. G. ÅSBRINK and A. MAGNELI, *Acta Chem. Scand.* **21** (1967) 1977.
4. D. GOLDBERG, *Rev. Int. Hautes Temp. Refract.* **5** (1968) 181.
5. R. D. SHANNON, *Acta Crystallogr.* **A32** (1976) 751.
6. Powder Diffraction File, Card No. 26–40, Joint Committee on Powder Diffraction Standards, Swarthmore, USA.
7. K. SCHWARZ and A. NECKEL, in 2nd Int. Conf. Science Hard Mater. Rhodes, September 1984 (Inst. Phys. Conf. Ser. 75) edited by E. A. Almond and R. Warren (Adam Hilger, Bristol, 1986) p. 45.

Received 2 November 1989
and accepted 1 March 1990