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Chemical and microstructural investigations of high-temperature interactions between AlN and TiO_2*

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Chemical and microstructural changes occurring when AlN and TiO_2 are put in contact at 1400 to 1600° C in nitrogen have been studied. Experiments were carried out with single-crystal TiO_2 embedded in AlN powder compacts, and with AlN + TiO_2 powder mixtures of varying relative proportions. A displacement type of reaction is shown to take place yielding Al_2O_3 + TiN, with an intermediate step when a reduced titanium pseudobrookite $(Al, Ti)_2TiO_5$ phase is generated and subsequently tends to disappear. For appropriate AlN/TiO_2 initial ratios, a fine homogeneous two-phase composite microstructure may be obtained between Al_2O_3 and TiN reaction products.

1. Introduction

Several technically important compounds may be obtained by combining two of the four elements aluminium, titanium, oxygen and nitrogen. Furthermore, a number of condensed phases are known, in which any three of these four species are associated [1–5]. In some instances, however [1–3], the latter are thermodynamically stable at high temperature only, which suggests that they may be stabilized by the entropy contributions to their free energies. If such were the case, it might be argued that dissolving appropriate foreign elements might bring further improvements in the thermodynamic stabilities of the corresponding ceramic alloys.

A possible illustrative example is aluminum titanate, Al_2TiO_5, which crystallizes in the pseudobrookite structure and has been observed to decompose into Al_2O_3 + TiO_2 at temperatures somewhat below 1300° C [6]. Various cations have been shown to be substitutionally soluble in the aluminium titanate structure up to substantial levels [7, 8] and in some cases the decomposition temperature was claimed to have been markedly reduced [8]. Although other effects, such as the development of internal stress fields in polycrystalline ceramics, may also influence the observed decomposition temperature, such findings do go along with the above entropy assumption.

The present work therefore has been undertaken with the following two objectives in mind. On the one hand, it was to be an attempt to prepare condensed phase(s) from aluminium, titanium, oxygen and nitrogen if such phases may at all exist. On the other hand, particular attention was to be given to the possibility of obtaining an aluminum titanium oxynitride with a pseudobrookite structure, by substitutions in

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the anion sublattice rather than in the cation sublattice as was done previously. For experimental simplicity, the investigation was restricted (as a first step) to studying the high-temperature interactions between AlN and TiO_2 starting materials, together with the resultant microstructures, either in reaction couples between TiO_2 single crystals and AlN powder compacts, or in various compacted and sintered powder mixtures.

2. Experimental procedures

Commercially available AlN (Ventron GmbH, Karlsruhe, FRG) and TiO_2 (Tioxide Ltd, Stockton-on-Tees, UK) were used having nominal purities of 99% and 99.9% respectively, according to the suppliers. Verneuil-grown rutile single crystals were also obtained (Nakazumi, Osaka, Japan). Reaction couples between diamond-polished single-crystal TiO_2 pieces embedded in AlN powder were made by vacuum hot pressing in a graphite die for 15 min at either 1400 or 1850° C. The latter was subsequently annealed for 72 h at 1400° C in flowing nitrogen. On the other hand, powder mixtures were prepared having different ratios of AlN and TiO_2 by milling for 24 h with isopropanol in an alumina ball-mill. After drying and screening, the powders were cold-pressed to 200 MPa and sintered from 1 to 44 h at 1400° C or for up to 48 h at 1600° C respectively. In all cases the pellets were placed in alumina crucibles and completely surrounded by a tapped AlN powder shell. Such set-ups were fired in an Al_2O_3 tube furnace in nitrogen atmosphere flowing at a rate corresponding to about six renewals per hour. The O_2 partial pressure of the inflowing gas ($\sim 10^{-20}$ atm) was measured with a ZrO_2 cell, and found to increase up to 10^{-10} atm at the tube outlet after a few hours of heat treatment.

The overall chemical changes taking place within the powder mixtures were assessed by recording their X-ray diffraction patterns in a Guinier camera with Cu*Kα* radiation. In some cases thermogravimetric analysis (TGA) runs were carried out under purified argon in a Mettler thermal analyser. It was verified on a few pellets sintered in argon rather than nitrogen that qualitatively similar results were obtained with respect to the course of reactions taking place in the various mixtures. Such was also proved to be the case with samples vacuum hot-pressed in graphite dies for 15 min at 1400° C.

Both the chemical and conventional phase distribution microstructures were observed on diamond-polished surfaces with an electron probe microanalyser (EPMA) and with scanning (SEM) or optical microscopes respectively. The EPMA was operated under 10 kV and 125 nA. It provided qualitative information on the presence of all four elements independently, through their characteristic *Kα* lines, and more quantitative data on aluminium and titanium concentrations. Finally, it seems worth mentioning that special care was taken to avoid confusing Ti*Ll* photons with N*Kα* ones which have nearly the same energy.

3. Results and discussion

From many different AlN + TiO_2 powder mixtures three have been investigated in more detail, i.e. "M11" = $2TiO_2 : 1AlN$, "M12" = $1TiO_2 : 2AlN$, and "M15" = $1.5TiO_2 : 2AlN$ based on the following considerations. An *a priori* formula for a hypothetical N-pseudobrookite phase would be $AlTi_2O_4N$, in which all titanium should be in the +4 state. Such a formula corresponds to M11. Similarly, an *a priori* formula for a hypothetical aluminum titanium oxynitride spinel phase would be $Al_2TiO_2N_2$, corresponding to M12. Finally, M15 was investigated on the assumption (which turns out to be confirmed by experimental observation) that a displacement reaction $AlN + TiO_2 \rightarrow Al_2O_3 + TiN$ could take place. A similar type of reaction was found to occur in the Si–Al–O–N system under appropriate conditions [9], i.e.

$$4AlN + 3SiO_2 \rightarrow 2Al_2O_3 + Si_3N_4$$

3.1. Chemical transformations

Table I summarizes the qualitative X-ray phase analyses of sintered and annealed samples. Fig. 1 shows typical diffraction patterns for these three compositions, after heating several hours at 1400° C in nitrogen. No attempt was made at this stage to precisely quantify either the time evolutions of the relative amounts of the various phases detected, or their lattice parameters. Several important points however can be made on the basis of these results:

(a) In all mixtures, α-Al_2O_3 and titanium nitride have been produced after one hour at

TABLE I Qualitative distribution of phases in AlN + TiO_2 mixtures after heat treatment

initial composition	Phases observed after heat treatment at 1400° to 1600° C		
$2TiO_2:1AlN$	Pseudobrookite (vs)*,	TiN (m)	Al_2O_3 (w)
$1TiO_2:2AlN$	TiN (vs),	Al_2O_3 (m),	AlN (w to m)
$1.5TiO_2:2AlN$	TiN (vs),	Al_2O_3 (vs),	Pseudobrookite (w)*

*Relative intensity decreases with time and/or temperature.

1400° C, and persist for all longer and/or higher temperature heat treatments.

(b) In M12, titanium dioxide has been entirely eliminated whereas some unreacted AlN is still present. This proves that under the present conditions, M12 does not yield a nitrogen spinel as had been hypothesized. It also confirms that AlN is compatible with the other phases present, i.e. Al_2O_3 [3] and TiN [5].

(c) In the other two compositions (M11 and M15), which are initially higher in TiO_2, both the initial compounds have disappeared, but a third phase with a pseudobrookite structure (Fig. 1) has been formed together with TiN and Al_2O_3. Comparison with a reference aluminum titanate spectrum definitely shows that the composition of this phase does not correspond to Al_2TiO_5. It is also to be noted that, contrary to Al_2O_3 and TiN, it may not be stable. It has a definite tendency to disappear upon long term annealing, especially in M15 which initially contained less TiO_2 than M11.

A first conclusion then to be drawn at this stage is that a displacement reaction tends to take place in AlN + TiO_2 powder mixtures, but it is not straightforward and probably involves at least one intermediate or parallel reaction in which a pseudobrookite type of compound is formed.

The TGA recordings obtained with 6° C min^{-1} heating rate (Fig. 2) provide supplementary

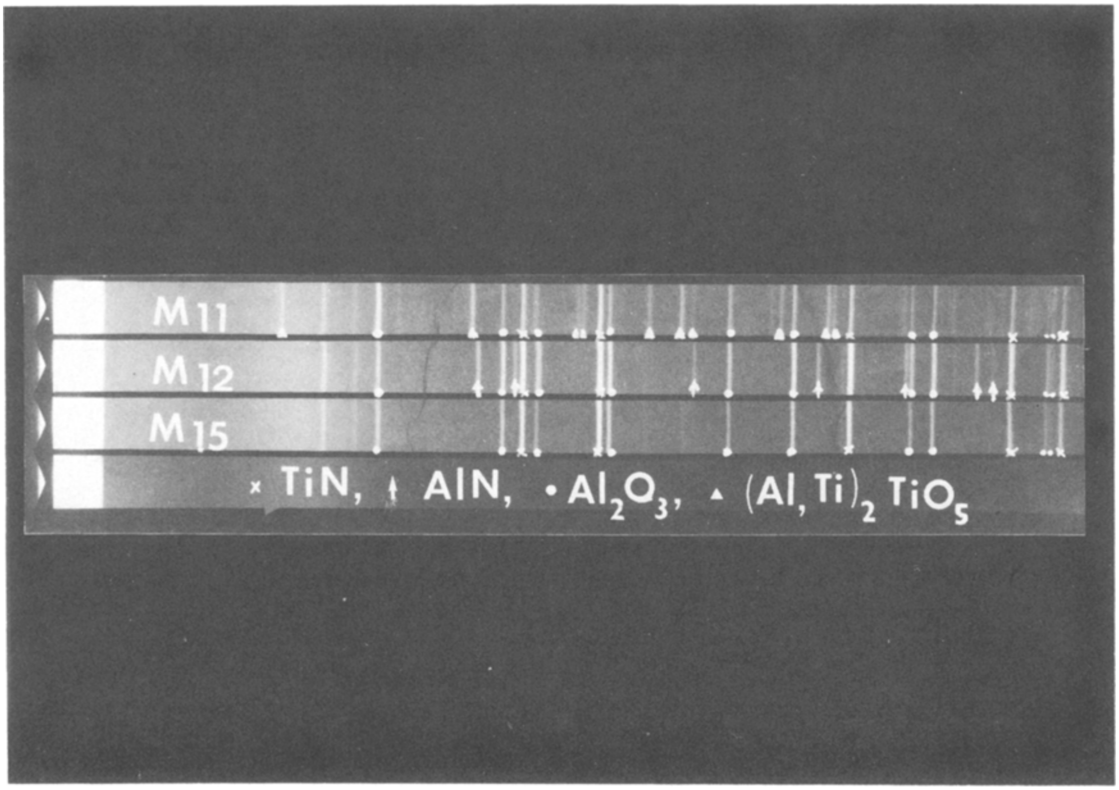
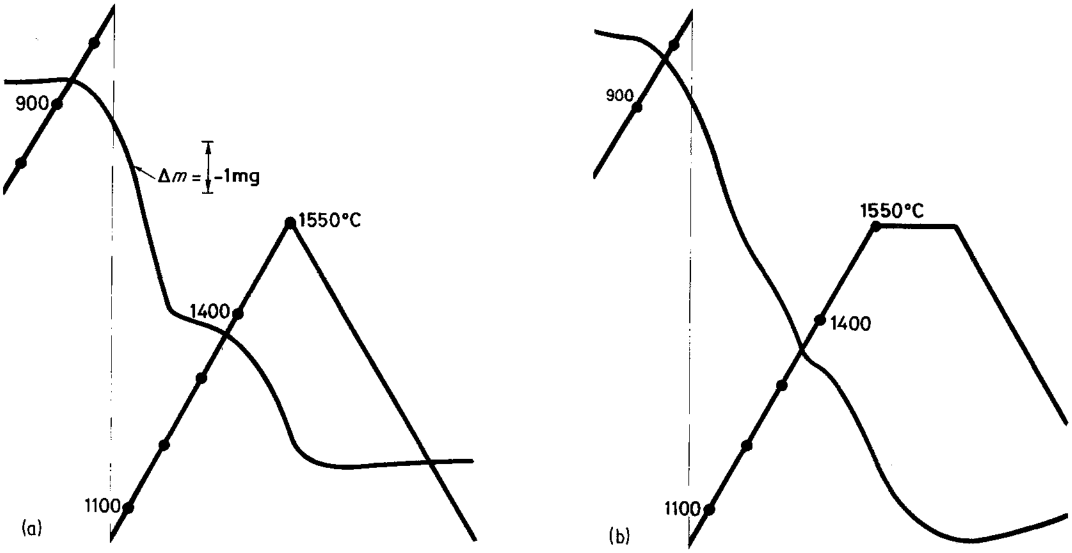


Figure 1 X-ray powder patterns of AlN + TiO_2 mixtures, heat treated for a few hours at 1400° C.



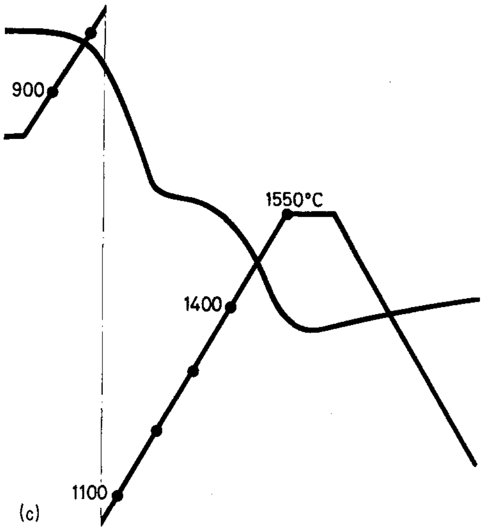


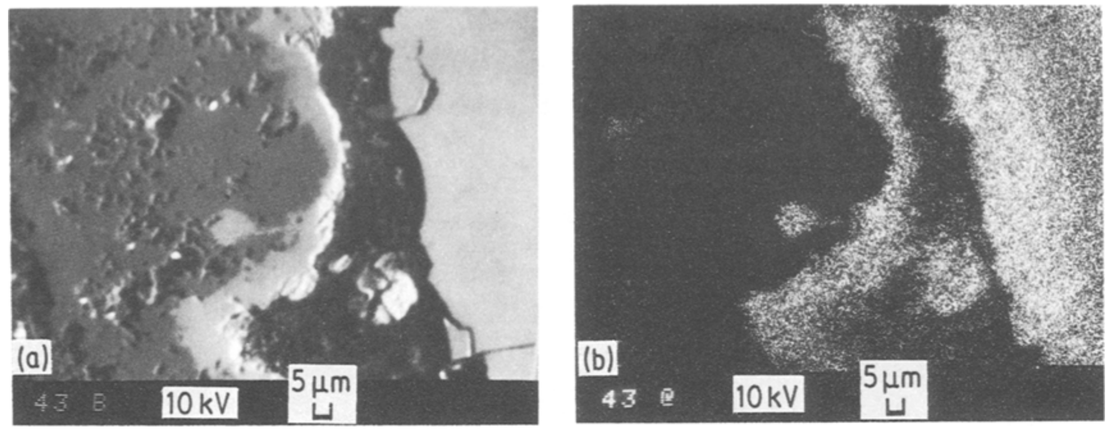
Figure 2 Thermogravimetric recordings of AlN + TiO_2 mixtures under constant heating rates in argon: (a) 1.5 TiO_2 : 2 AlN, 180 mg; (b) 2 TiO_2 : 1 AlN, 163 mg; (c) 1 TiO_2 : 2 AlN, 168 mg.

information on several other points. On the one hand they show that the system starts reacting at 950 to 1000° C, with a loss of weight presumably due to some gas evolution. The latter is unlikely to be pure oxygen since at these temperature levels it could oxidize AlN powder [10]. X-ray diffraction from samples of TGA runs interrupted at 1250° C failed to reveal any TiN. The initial reaction step thus involved the oxidation of some AlN by TiO_2, with the corresponding transfer of titanium in the +3 state and nitrogen evolution. This in turn favours the formation of the pseudobrookite phase, the composition of which is to be discussed below. On the other hand, Fig. 2 also shows that as temperature increases beyond ~ 1350° C a further loss of weight is recorded, to which a contribution must be made by the formation of titanium nitride. More systematic experiments obviously would be needed in order to clarify whether TiN derives from the gradual conversion of titanium suboxides (no X-ray pattern of an NaCl-type TiO_xN_y phase could however be detected), or whether it is produced concurrently with the decomposition of the previously formed pseudobrookite phase, or both. The scenario may well be different depending upon the initial overall composition of the powder mixture.

Inasmuch as the pseudobrookite phase may be considered either as unstable or transient, then an overall chemical balance equation may be written for the AlN–TiO_2 system in the temperature and time ranges considered here:

$$\lambda TiO_2 + 2AlN \rightarrow Al_2O_3 + \lambda TiN + \left(1 - \frac{\lambda}{2}\right) N_2 + (\lambda - \tfrac{3}{2})\, O_2$$

where $\lambda (> 0)$ is a parameter describing the composition of the initial powder mixture. From thermochemical tables, the corresponding free energy change for the above reaction would be $\Delta G \approx -100$ kJ and -81 kJ for $T = 1500$ and 2000 K respectively, when $\lambda = 3/2$, for



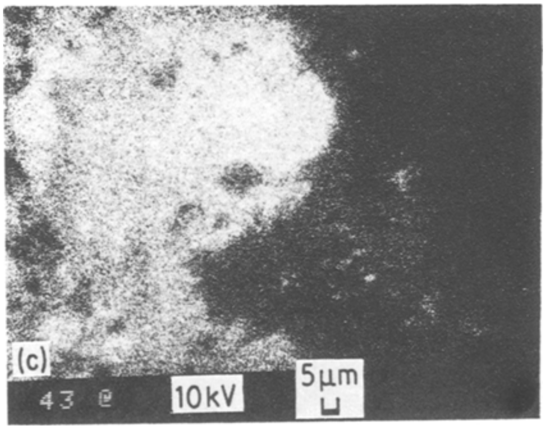


Figure 3 Microstructure of interface region of single-crystal TiO_2 + AlN powder reaction couple, hot pressed 15 min at 1450° C: (a) backscattered electrons SEM image, (b) Ti$K\alpha$ image, (c) Al$K\alpha$ image.

$p_{O_2} \ll p_{N_2}$ and $p_{N_2} \approx 1$ atm (≈ 0.1 MPa). The present experiments may be compared with this overall equation. Our composition M15 would correspond to $\lambda = 3/2$ and give rise to a theoretical relative weight loss $\Delta m/m \approx -3.5\%$ instead of a measured -4% (Fig. 2).

Compositions M12 and M11, which would in principle correspond to $\lambda = 1$ and $\lambda = 4$ respectively, cannot directly be reconciled with the above theoretical overall balance. The reasons are that either an extra oxygen supply would be needed for the balance to be fulfilled (M12), which is inconsistent with the chosen operating conditions, or the overall relative weight loss (M11) should amount to $\sim 12.9\%$, much too high compared with experiment (Fig. 2). It is therefore believed more realistic to view the M12 and M11 compositions with reference to M15 as follows:

$$\mathrm{M12} = \mathrm{M15} + 1\mathrm{AlN}$$

$$\mathrm{M11} = \mathrm{M15} + 2.5\mathrm{TiO_2}$$

In the former case, unreacted AlN should be observed together with Al_2O_3 and TiN, which is confirmed by X-ray analyses. Also, the corresponding theoretical weight loss (-3.15%) is close to the observed -3.3% (Fig. 2). In the latter case, since no TiO_2 is retained, it must be admitted that the overall weight change in M11 should result from the partial reduction of the extra $2.5TiO_2$ bringing about some oxygen loss. If the resulting titanium suboxides are taken as Ti_3O_5 and Ti_2O_3 respectively, then the corresponding theoretical weight changes in M11 should be -5.1% and -6.7% respectively, to be compared with a measured -5.8%.

3.2. Microstructural observations

All microstructrual evidence, collected either from reaction couples between TiO_2 single crystals and compacted AlN powder or from sintered powder mixtures, is in accord with the above interpretation scheme for chemical changes affecting the AlN–TiO_2 system. Fig. 3 shows an SEM micrograph and characteristic elemental X-ray images of the interface region in a reaction couple hot-pressed to 1450° C for 15 min. It is apparent that no cohesion developed between the TiO_2 single crystals and its surrounding AlN powder compact, suggestive of some local gas evolution. It is also seen that some intermediate layer was formed containing both aluminium and titanium, but due to its small thickness it was not possible to unambigously assess its composition.

Upon prolonged heat treatment under

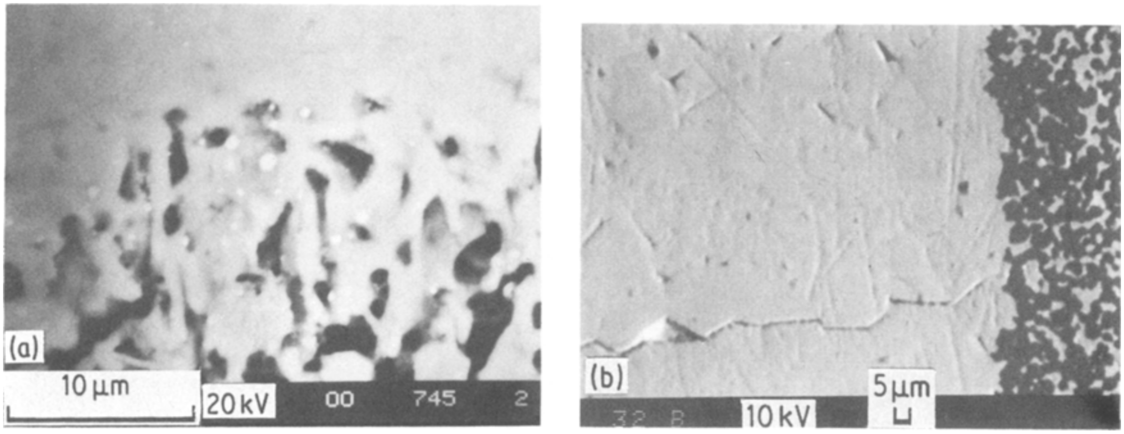


Figure 4 Microstructure of interface region of single crystal TiO_2 + AlN powder reaction couple, hot pressed 15 min at 1850° C and annealed 72 h at 1400° C: (a) AlN side with evidence of a porous zone near the interface; (b) former TiO_2 side, with evidence of a fine two-phase region near the interface.

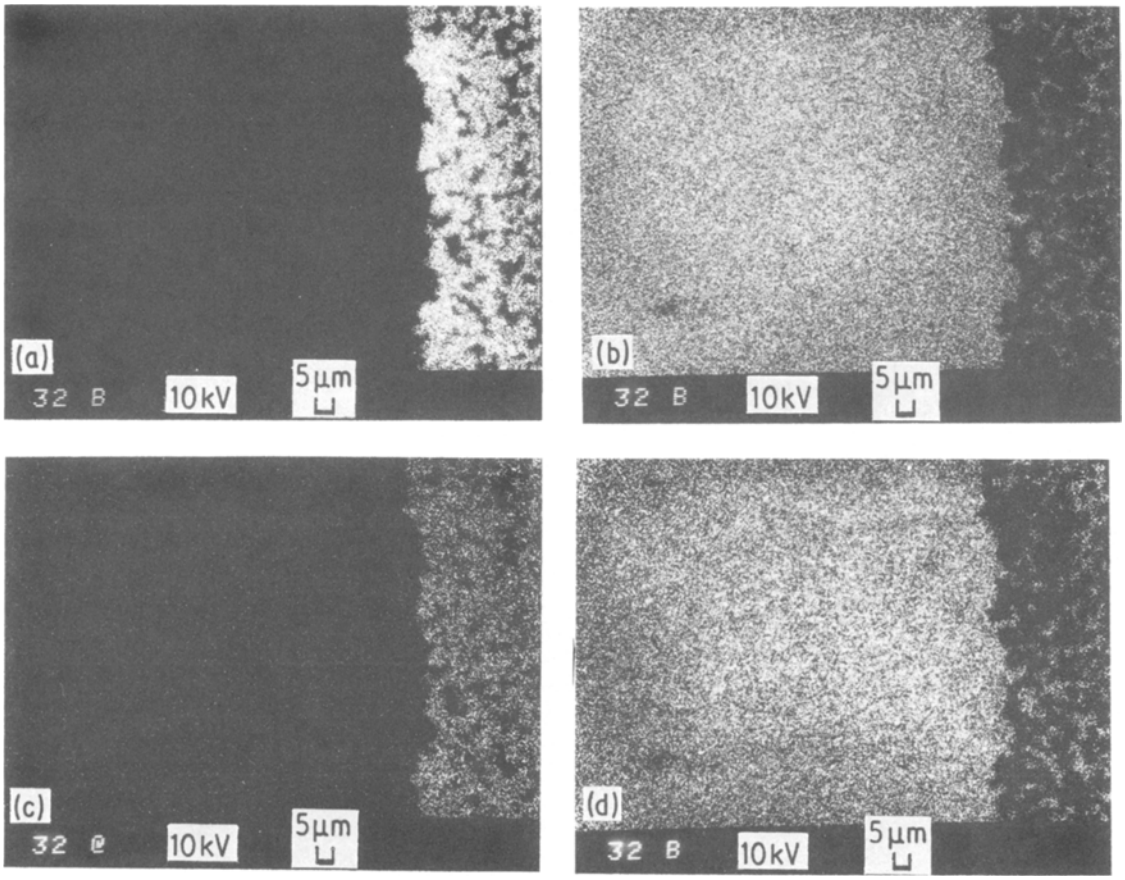


Figure 5 Elemental X-ray *Kα* images of interface region near the former TiO_2 side shown on Fig. 4b (a) aluminium, (b) titanium, (c) oxygen, (d) nitrogen.

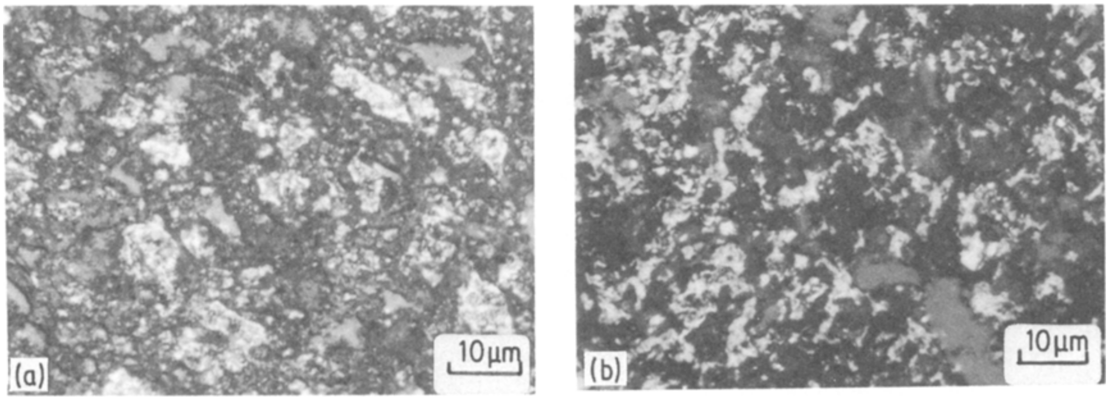


Figure 6 Microstructures of TiO_2 : 2AlN powder mixtures: (a) after 1 h at 1400° C, (b) after 24 h at 1600° C.

conditions approximating those of a closed system (Fig. 4, showing a densified AlN outer shell), a clear representation of the overall reaction scheme becomes apparent. On the one hand a porous layer is seen in the vicinity of the interface within the otherwise densified AlN field, indicating that most gaseous species are generated and/or collected there. Moreover, all evidence for an intermediate layer has now disappeared (Fig. 4), and a peculiar two phase microstructure has developed on a fine scale within the original rutile crystal. The characteristic elemental X-ray images (Fig. 5) show it to be a mixed Al_2O_3 + TiN layer, whereas the core of the former TiO_2 crystal has entirely been converted into TiN.

The microstructures of sintered AlN + TiO_2 mixtures also display some interesting features (Figs. 6–8). In M12 compositions, rather coarse and irregular structures are obtained (Fig. 6) and significant amounts of residual porosity may be noted. In M11 samples a three-phase assemblage is evident, the scale of which appears not to be greatly affected by annealing time and/or temperature (Fig. 7). It consists in a matrix which according to X-ray evidence (Table I, Fig. 1) should be the pseudobrookite phase, and two dispersoids which often appear in association. Electron probe microanalysis has confirmed the latter to be Al_2O_3 and TiN respectively, whereas the matrix contains aluminium, titanium and oxygen. But no significant nitrogen concentration could be detected above the NK_α background. It is thus to be concluded that the M11 matrix is a reduced titanium pseudobrookite with formula $(Al_xTi^{3+}_{1-x})_2Ti^{4+}O_5$. Characteristic Al : Ti EPMA intensity ratios (referred to Al_2O_3 and TiO_2 standards) yield an x value of ~0.3. Finally, the M15 samples exhibit substantially finer microstructures than those obtained from other compositions do (Fig. 8) for equivalent heat treatments. As expected, they tend to retain only Al_2O_3 and TiN domains with a low residual

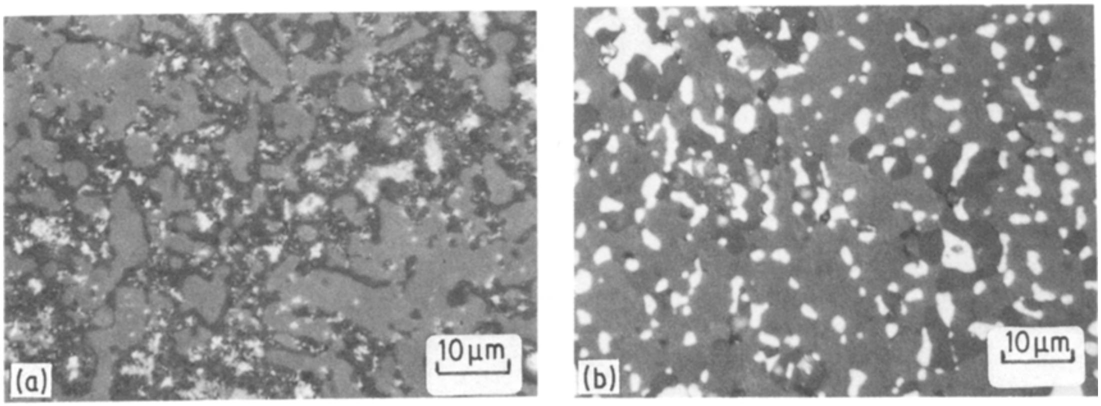


Figure 7 Microstructure of $2TiO_2$: AlN powder mixtures: (a) after 1 h at 1400° C, (b) after 24 h at 1600° C.

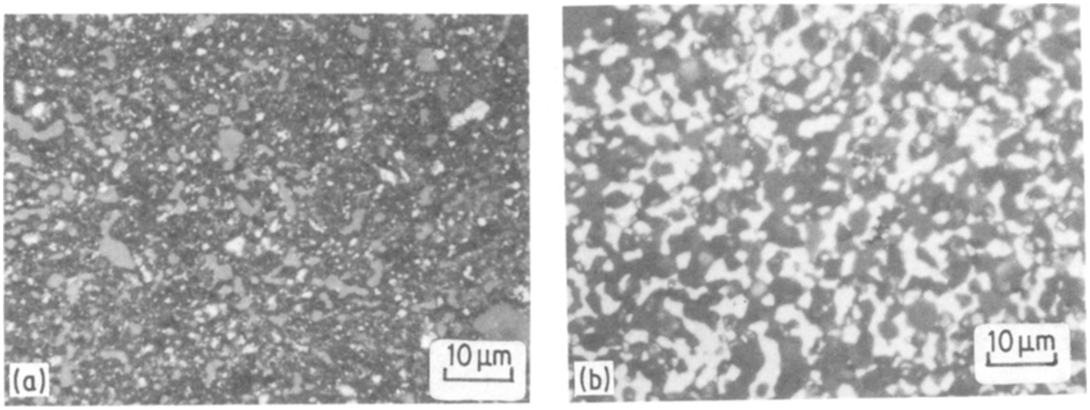


Figure 8 Microstructures of $1.5\,TiO_2 : 2AlN$ powder mixtures: (a) after 1 h at 1400° C, (b) after 24 h at 1600° C.

porosity. It is possible that porosity was eliminated after completion of the reaction by straight sintering, in particular within the Al_2O_3 skeleton.

4. Conclusion

Under the present experimental conditions it has been observed that solid TiO_2 oxidizes AlN into Al_2O_3 with the corresponding evolution of nitrogen and formation of titanium suboxide(s). An aluminium titanate pseudobrookite phase is then formed with a high proportion of titanium in the +3 state occupying aluminium sites. No conclusive evidence was however found for the presence of nitrogen in such a phase, which tends to disappear upon longer-term and/or higher-temperature annealing. The end products of the reaction are Al_2O_3 and TiN, possibly found with secondary phases such as unreacted AlN, depending upon initial composition when working with powder mixtures. The overall behaviour therefore appears to be that of a displacement or metathesis reaction. When appropriate proportions of AlN and TiO_2 powders are mixed together a fine and homogeneous codispersion of the resulting Al_2O_3 and TiN phases may be obtained by reaction sintering in nitrogen. The corresponding bodies also exhibit little residual porosity.

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