JOURNAL OF MATERIALS SCIENCE 27 (1992) 1129–1135

Investigation of the displacement reaction in mixed AlN+TiO$_2$ powders

Part II *Atmosphere effects*

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Following previous work (reported in Part I) on the reactions within compacts of mixed AlN + TiO$_2$ particles, the effects of changing the effective nitrogen pressure imposed to the system are investigated. Either increasing it (to 10^2–10^3 atm) or decreasing it (to 10^{-2}–10^{-3} atm) is shown to somewhat simplify the overall chemical scheme while also having an influence upon the development of microstructures. At high p_{N_2} AlN is passively oxidized and TiO$_2$ is reduced to Ti$_4$O$_7$ or Ti$_3$O$_5$ with limited Al$_2$O$_3$ dissolution into them before they get nitrided into TiN. At low p_{N_2} AlN is actively oxidized with copious Al transport toward Ti oxides via the gas phase. Simultaneously, TiO$_2$ is reduced to Ti$_2$O$_3$ which can be nitrided therefrom. In all cases TiN is also formed on AlN particles, following gas-phase transport of molecular TiO. The kinetics of the overall process is not limited by AlN oxidation except at high applied N$_2$ pressures. Varying the initial relative AlN–TiO$_2$ composition from the basic 2:1.5 molar ratio brings about no novelty in the nature of solid phases being formed or in the general course of events in the temperature range investigated here, i.e. $T < 1800$ K.

1. Introduction

In the preceding paper [1], hereafter referred to as Part I, the displacement reaction in various 1.5TiO$_2$ + 2AlN compacted powder mixtures, heat-treated under 1 atm N$_2$ pressure, has been studied from the point of view of microstructure development. Particular attention was paid to identifying the detailed sequence of appearance and disappearance of solid phases, and their locations with respect to each other in the reacting medium. Thus a consistent picture of the course of events could be obtained, with the more or less explicit assumption that only N$_2$ and O$_2$ partial pressures needed be known to interpret the observations. In other words, considering only the respective O$_2$ and N$_2$ pressures locally existing at the sites of reactions was found sufficient to qualitatively understand individual elementary steps of the overall reaction and follow their sequence, as if thermochemical equilibrium remained close to being achieved at all times. Such a presentation, which also amounts to assuming that the kinetics of the process results only from matter transfers within solid phases, is oversimplified as already pointed out in the conclusion to Part I. In particular, the possibility that Al- and/or Ti-containing species may be transferred via the gas phase, thus contributing somewhat to the overall mechanism, was not considered despite some direct microstructural evidence.

In the present paper, therefore, a complementary analysis of the displacement reaction between AlN and TiO$_2$ will be presented based on experiments performed under imposed nitrogen pressures markedly different from the previously chosen conditions of 1 atm. Both reduced and increased pressure conditions have thus been investigated. Since on the other hand the overall reaction balance involves some N$_2$ outgassing [1], it could be reasoned that maintaining a reduced N$_2$ pressure in contact with the reacting medium should speed the kinetics up, whereas increasing it should have the converse effect. It is also an objective of this paper, therefore, to qualitatively evaluate such effects, it being kept in mind that they might be overshadowed by the fact that the effective O$_2$ and N$_2$ partial pressures within the reacting porous media are not accessible experimentally and could be quite different from those predicted by equilibrium thermochemical calculations.

2. Experimental procedure

The starting AlN and TiO$_2$ materials and the sample preparation techniques have already been described [1] as well as those for characterizing the microstructures and solid-phase content of the reacted materials after cooling down to room temperature. The heat-treatments, however, were varied as mentioned and Table I summarizes the essential conditions which were resorted to for carrying out such treatments. The same temperature range as before was again investigated, i.e. 1400–1800 K.

TABLE I Heat-treatment conditions

Crucible	Furnace N_2 pressure (atm)	Type of gas buffer	Calculated p_{O_2} (equil. 1500 K) (atm)	Heating rate (K h^{-1})
Al_2O_3	1	Flowing N_2	10^{-6} (supplier)	7000
Niobium	5×10^{-7}	Nb-NbO-Nb_2O_5	10^{-22}	10-600
Graphite (sinter-HIP)	100	C-CO-CO_2	10^{-21}	500-1000

3. Results and discussion

Consideration of the oxynitriding reaction

$$2AlN + \tfrac{3}{2}O_2 \rightleftharpoons Al_2O_3 + N_2$$

shows that in equilibrium at a given temperature, increasing the nitrogen pressure will bring about a corresponding increase in p_{O_2}, and vice versa. A tendency should therefore ensue for Magneli phases Ti_nO_{2n-1} with higher n values to be either stabilized or get nitrided directly, and vice versa. More precisely, the stability fields of the various solid phases possibly to be found in the system have been calculated from data in JANAF Tables [2] and are represented in Figs 1 and 2. The former diagram locates the AlN-Al_2O_3 equilibrium at different N_2 pressures with respect to the stability fields of titanium oxides as a function of reciprocal temperature. The latter diagram in turn delineates the p_{N_2}-p_{O_2} conditions under which a given Magneli phase Ti_nO_{2n-1} may be directly nitrided into TiN in the temperature range 1300-1800 K. Vertical segments, in Fig. 2 in particular, outline boundaries between different suboxides of titanium. Such a thermochemical framework provides a helpful reference to interpret experimental observations as will now be shown.

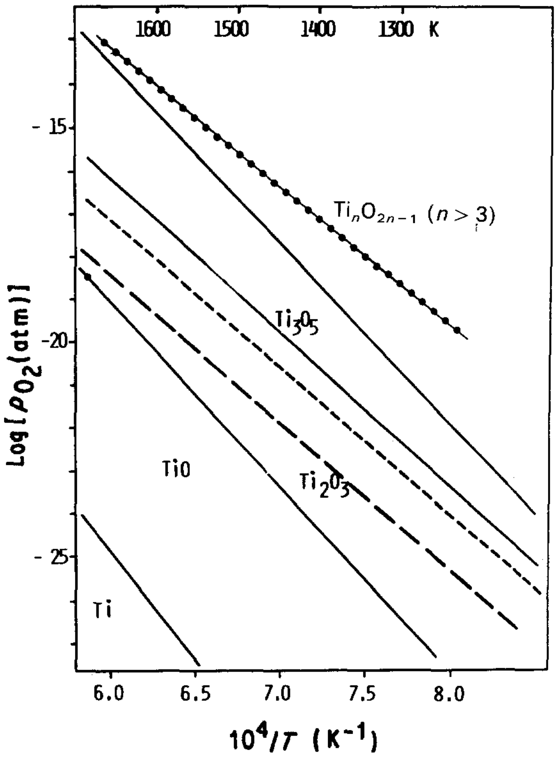

Figure 1 Equilibrium p_{O_2}-T diagram of solid phases in the Ti-O system, relative to the AlN → Al_2O_3 reaction. Continuous lines correspond to boundaries between stability fields of successive Ti_nO_{2n-1} phases, whereas dotted and dashed lines refer to the AlN = Al_2O_3 equilibrium under various applied N_2 pressures. p_{N_2} (atm): (-●-)10^3, (---)10^{-2}, (--)1.

3.1. Reaction under high N_2 pressure

The same types of powder compacts as before [1] were heat-treated in a sinter-HIP furnace under nitrogen pressures ranging from 200 to 1000 atm. Fig. 3 shows a typical X-ray diffraction pattern of an initially fine particle mixture (FF) recorded after cooling down to room temperature. The corresponding sample had been heat-treated 1.5 h at 1400 K under 200 atm N_2. The reaction appears not to be complete, as besides

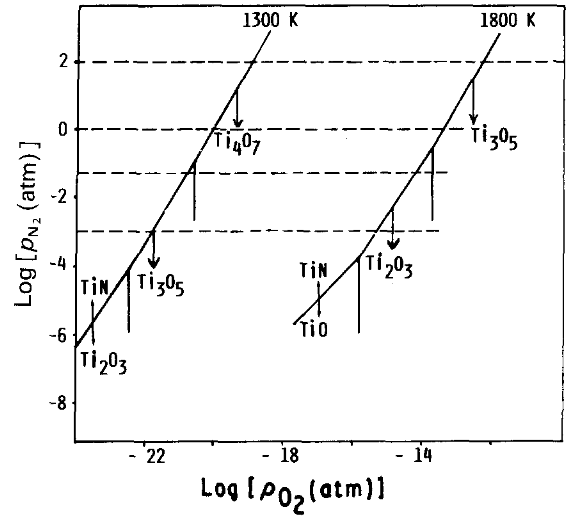

Figure 2 Equilibrium p_{O_2}-p_{N_2} diagram between solid TiN and titanium oxide Magneli phases in the T = 1300-1800 K range.

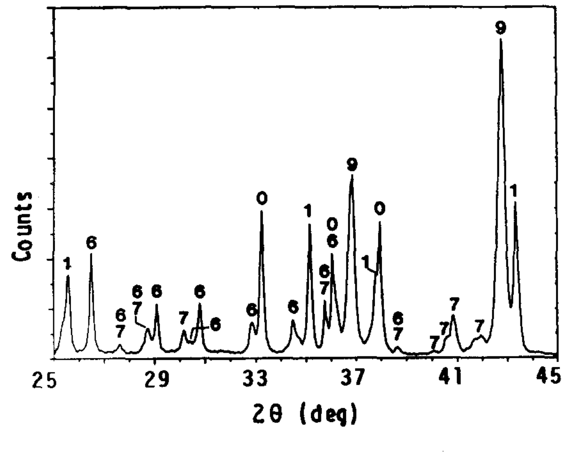

Figure 3 X-ray diffraction pattern of fine particle mixture after 1.5 h reaction at 1400 K and 200 atm N_2 pressure. Line identification: (0) AlN, (1) Al_2O_3, (6) Ti_5O_9, (7) Ti_6O_{11}, (9) TiN.

AlN and Al_2O_3, both Ti_6O_{11} and Ti_5O_9 can be detected as well as TiN. Generally speaking, no lower oxide than Ti_4O_7 could be detected in all experiments carried out at > 100 atm N_2. Thus the formation of pseudo-brookite or Ti_3O_5 solid solutions [1] could be bypassed in the present conditions, and the Ti_nO_{2n-1} phase with the lowest n observed depended on both T and p_{N_2}, e.g. $n = 5$ for 1400 K and 200 atm, $n = 4$ for 1450 K and 200 atm or 1600 K and 1000 atm. It is also to be pointed out that under the present conditions neither the AlN nor the TiO_2 particle sizes were found to affect these lower n values.

The microstructures in various combinations of AlN–TiO_2 relative sizes are exemplified by Fig. 4, obtained after 3 h reaction at 1600 K and 10^3 atm N_2. In CC samples made from initially coarse TiO_2 single-crystal chips and large AlN particles [1], unreacted Ti_4O_7 cores are clearly visible whereas they have disappeared from CF samples prepared with fine AlN powder. Thus, in contrast to the $p_{N_2} = 1$ atm case [1] the AlN particle size does appear to play a role in the reaction kinetics when the nitrogen pressure is increased. Also markedly different from previous findings are the lack of evidence of significant Al or Ti vapour transport (no Al_2O_3 or TiN shells on former TiO_2 or AlN particles, respectively), and the lack of elemental Al in former TiO_2 particles as revealed by electron probe microanalysis (EPMA). The composite structure, seen to progress from the outer surface to the interior of former TiO_2 particles (Fig. 4), consists of TiN with a finely dispersed porosity arising from the large ($\sim 35\%$) relative molar volume change that takes place when a Ti suboxide is nitrided into TiN.

In conclusion, therefore, under high N_2 pressures the AlN–TiO_2 displacement reaction appears to proceed as was qualitatively anticipated from thermochemistry (Figs 1 and 2) and consists in only two essential steps: (i) reduction of TiO_2 to Ti_nO_{2n-1} where $n > 4$ and (ii) nitridation of Ti_nO_{2n-1} into TiN, while AlN is gradually oxidized *in situ*, i.e. outer layers of Al_2O_3 are visible on large AlN particles (Fig. 4a). The overall chemical balance may be written as follows for $n = 4$:

$$\text{(a)}\left[\begin{array}{l}\frac{3}{2}\,TiO_2 \rightarrow \frac{3}{8}\,Ti_4O_7 + \frac{3}{16}\,O_2\\ \frac{1}{4}\,AlN + \frac{3}{16}\,O_2 \rightarrow \frac{1}{8}\,Al_2O_3 + \frac{1}{8}\,N_2\uparrow\end{array}\right.$$

$$\text{(b)}\left[\begin{array}{l}\frac{3}{8}\,Ti_4O_7 + \frac{3}{4}\,N_2 \rightarrow \frac{21}{16}\,O_2 + \frac{3}{2}\,TiN\\ \frac{7}{4}\,AlN + \frac{21}{16}\,O_2 \rightarrow \frac{3}{4}\,N_2 + \frac{7}{8}\,Al_2O_3 + \frac{1}{8}\,N_2\uparrow\end{array}\right.$$

Both the initial AlN and TiO_2 particles do not appear to interact with each other except indirectly via the

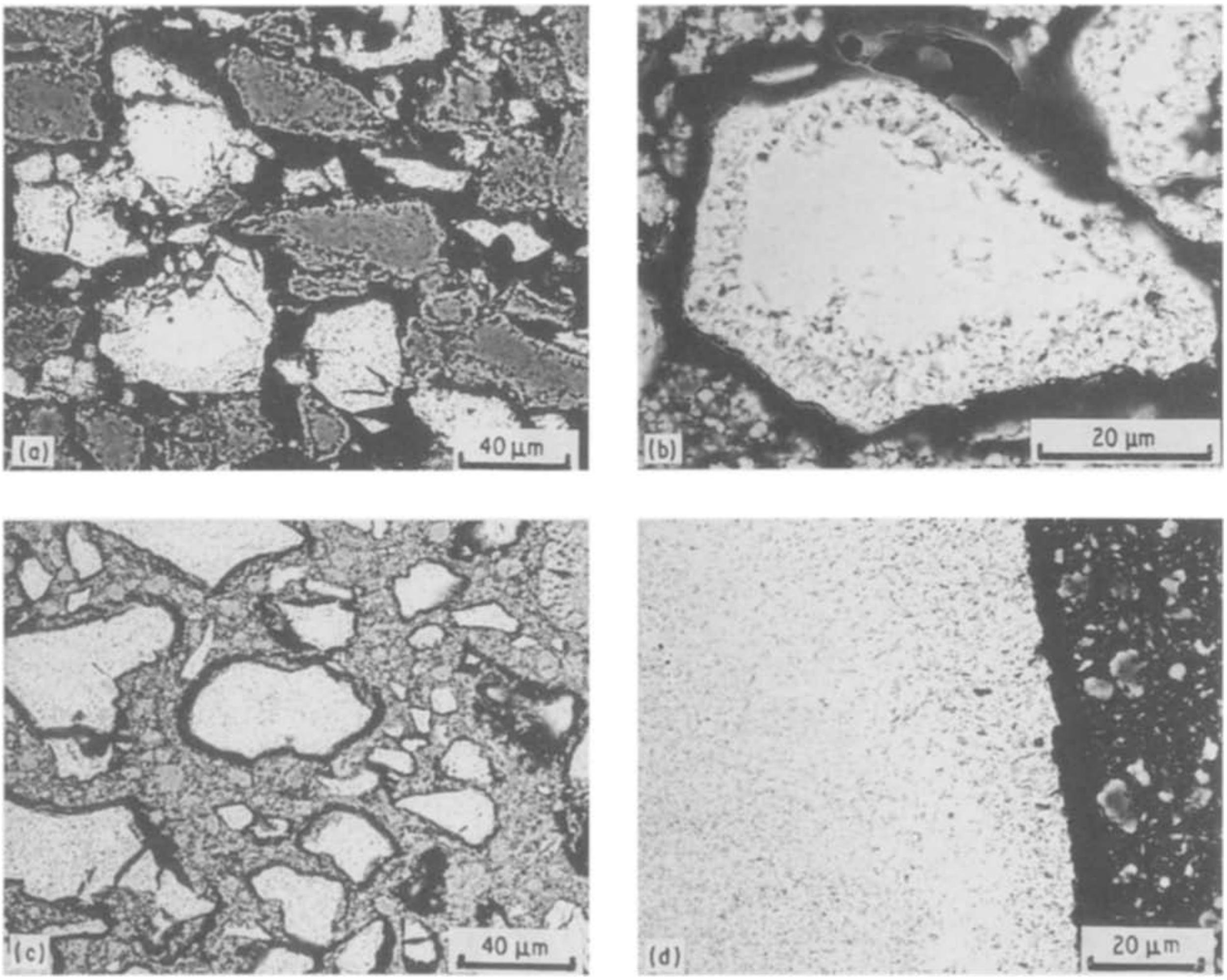

Figure 4 Examples of microstructures observed after 3 h reaction at 1600 K and 1000 atm N_2: (a) CC sample made from both coarse AlN and TiO_2 particles, (b) same as (a) at higher magnification, (c) CF sample made from coarse TiO_2 in fine AlN, (d) higher magnification of coarse former TiO_2 nitrided in fine AlN matrix.

coupled gaseous O_2 and N_2 exchanges. No microstructural refinement, as could be observed when an intermediate mixed Al–Ti oxide arises, is then possible here. The overall kinetics, which was not studied in detail, depends upon both AlN and TiO_2 initial particle sizes.

3.2. Reaction under low N_2 pressure

It should first be kept in mind that in practice the samples have been heat-treated in a vacuum furnace (Table I). Consequently, and because of the $\frac{1}{4}N_2$ liberated by the overall reaction, the effective N_2 pressures at the reaction sites within the compacted powder mixtures must have been intermediate between the residual furnace pressures ($\sim 10^{-7}$ atm) and that achieved when a 1 atm N_2 gas flow was maintained in the hot zone around the samples [1]. Effective *in situ* pressures are *a priori* functions of sample dimensions, pore geometries, i.e. respective particle sizes, and reaction kinetics. As a result they are not easy to estimate *a priori*.

Fig. 5 shows typical X-ray diffraction spectra obtained from partially reacted, coarse-grained (CC) samples, after 5 h at 1650 K (Fig. 5a) and after 2 h at 1500 K (Fig. 5b). Comparison between both spectra shows that

(i) TiO_2 can be reduced down to Ti_2O_3 before being nitrided into TiN, possibly with some residual oxygen still remaining in the NaCl lattice as EPMA analyses have shown.

(ii) More or less in parallel with the straight reduction to Ti_2O_3, a mixed $Al_xTi_yO_5$ phase with the α-Ti_3O_5 crystal structure [3] can be formed (and subsequently decomposed into $Ti_2O_3 + Al_2O_3$), thus showing that aluminium had been transported (presumably via the vapour phase) toward the Ti oxides in which it also went into solution as previously pointed out [1]. Similar behaviour is recorded with fine (FF) powder mixtures except that the Al content of their mixed $Al_xTi_yO_5$ phase is higher, everything else being the same. So, and as could be anticipated from consideration of their relative particle sizes, the effective N_2 pressure in FF samples is somewhat higher than in CC compacts.

Fig. 6 shows the kinds of microstructure which develop under low external pressure. Most of the features already noted when the reaction is performed under flowing 1 atm nitrogen [1] are again apparent here. In particular

(i) TiN shells develop around AlN particles. Their thickness tends to be somewhat larger under similar

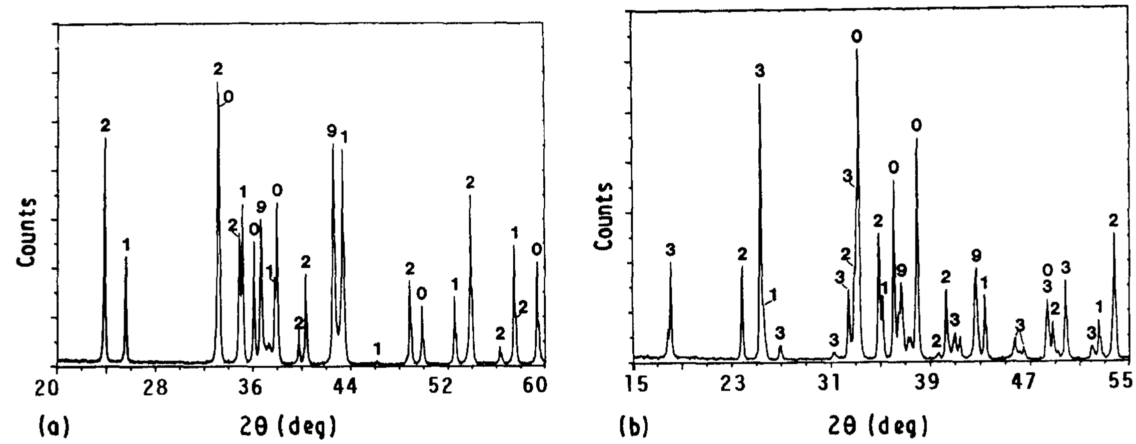

Figure 5 X-ray diffraction pattern of coarse particle mixtures after vacuum heat-treatment: (a) 5 h at 1650 K, (b) 2 h at 1500 K. Line identification: (0) AlN, (1) Al_2O_3, (2) Ti_2O_3, (3) α-Ti_3O_5, (9) TiN.

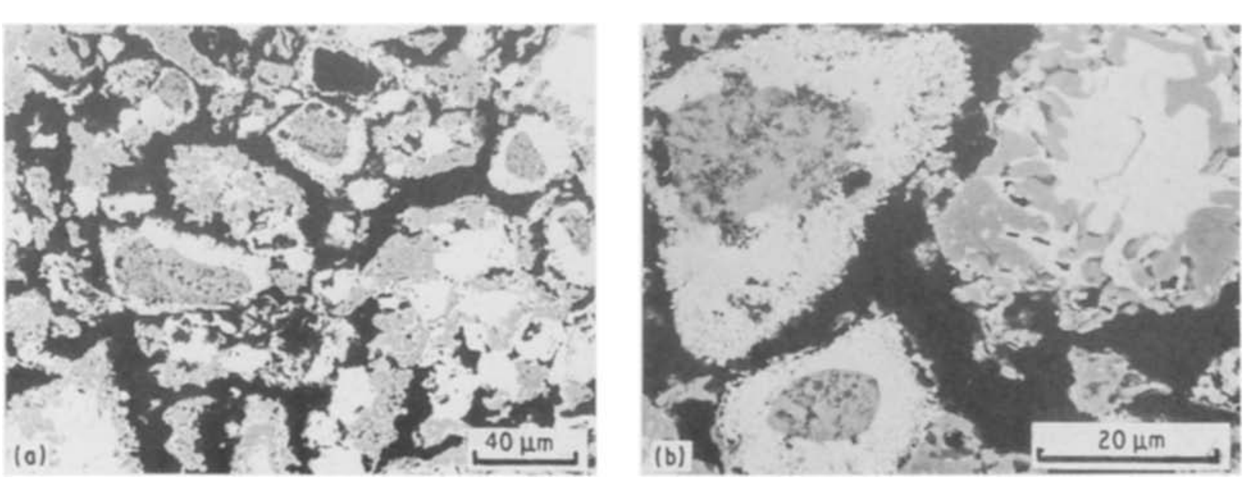

Figure 6 Examples of microstructures observed after reaction under reduced N_2 pressure in coarse powder mixture: (a) general aspect, (b) higher magnification showing porous AlN covered with TiN (left) and Al_2O_3 patches in Ti_2O_3 (right).

conditions, suggesting that the corresponding growth rate (through some sort of vapour transport) is greater when the effective N_2 pressure is decreased.

(ii) Tiny pores gradually develop within AlN according to a mechanism which has not been investigated. But it seems likely that Al is thereby extracted from AlN and subsequently deposited on to the reducing TiO_2 particles.

(iii) Al_2O_3 patches are easily seen in outer regions of the former TiO_2 particles. Their sizes, however, are larger than under conditions of flowing nitrogen [1] and they are not visible in the centres of large particles even when the latter have been nitrided, indicating that not enough aluminium was dissolved into the Ti_nO_{2n-1} phases before the latter were reduced to Ti_2O_3.

Referring now to Figs 1 and 2 as before, these show that since Ti_2O_3 can form and persist for some time in the system the effective O_2 pressure must have been reduced to appropriate levels, thus implying that the N_2 pressure in contact with AlN particles was in effect falling in the 10^{-2}–10^{-3} atm range for the temperature and particle size conditions of this study. Such levels appear sufficient (Fig. 2) for the conversion of Ti_2O_3 into TiN in the higher end of the temperature interval that was investigated. Since only limited amounts of $Al_xTi_yO_5$ mixed oxide are formed compared to the situation at higher N_2 pressure [1], particularly so when the TiO_2/AlN initial particle size ratio is large, then the resulting TiN phase appears more blocky and compact. The final microstructure is again coarser than under an applied 1 atm N_2 pressure. Finally, in the limiting case where the production and amounts of Ti_2O_3 remain large with respect to those of $Al_xTi_yO_5$, the overall chemical reaction scheme may again be considered to consist of two major steps:

$$\text{(a)}\quad \left[\begin{array}{l} \tfrac{3}{2}\,TiO_2 \rightarrow \tfrac{3}{4}\,Ti_2O_3 + \tfrac{3}{8}\,O_2 \\ \tfrac{1}{2}\,AlN + \tfrac{3}{8}\,O_2 \rightarrow \tfrac{1}{4}\,Al_2O_3 + \tfrac{1}{4}\,N_2\uparrow \end{array}\right.$$

$$\text{(b)}\quad \left[\begin{array}{l} \tfrac{3}{4}\,Ti_2O_3 + \tfrac{3}{4}\,N_2 \rightarrow \tfrac{9}{4}\,O_2 + \tfrac{3}{2}\,TiN \\ \tfrac{3}{2}\,AlN + \tfrac{9}{4}\,O_2 \rightarrow \tfrac{3}{4}\,N_2 + \tfrac{3}{4}\,Al_2O_3 \end{array}\right.$$

Such a formulation, it must once again be emphasized, is entirely schematical, and should not be taken as implying that the reaction atmosphere is only made up of nitrogen with small ($\sim 10^{-18}$–10^{-20} atm) amounts of oxygen. Indeed, thermochemical calculations (see Appendix) show that equilibrium partial pressures of such species as TiO, Al, Al_2O or AlO are many orders of magnitude higher than p_{O_2}. Their actual values during reaction obviously may be different, but it is interesting to recall that the Ti–O–N subsystem was found to evolve in a quasi-equilibrium fashion [1] whereas at low N_2 pressures the oxidation of AlN did not but none the less was not rate-controlling. It is thus felt that both Al and TiO vapour transport followed by their oxidation and nitridation at Ti oxide and AlN surfaces, respectively, can be invoked to rationalize the microstructural evolution at either site. A quantitative evaluation of the corresponding kinetics and the relative contributions of solid–gas versus solid–solid reactions would be beyond the scope of this paper. It is interesting to note in closing, however, that (see Figs A1 and A2 below) increasing the effective N_2 pressure imposed on the system should not substantially affect p_{TiO} but reduce p_{Al}, thus decreasing the tendency of AlN to oxidize via a gas–solid reaction, which is consistent with experiments reported above.

4. Conclusion

In addition to the previously reported [1] investigation of the $AlN + TiO_2 \rightarrow Al_2O_3 + TiN$ displacement reaction under flowing 1 atm N_2 pressure, experiments have been carried out under different imposed nitrogen pressures. The same kinds of compacted powder or particle mixture and temperature and time conditions as before have been used. It is found that both under high (10^2–10^3 atm) and low (10^{-2}–10^{-3} atm) effective nitrogen pressures, the evolutions of solid phases present in the system appears geared by the conditions under which AlN is oxidized, and kinetically limited by changes taking place within the former Ti oxide particles. Significant contributions to the overall chemical process may arise from transport of TiO and Al via the vapour phase. The former is roughly independent of the applied nitrogen pressure while the latter is not. At high p_{N_2} AlN is passively oxidized and very limited Al gas transport takes place, whereas at low p_{N_2} AlN is actively oxidized and a large fraction of the resulting Al_2O_3 at or in the former TiO_2 particles is due to such a gas–solid reaction. Similarly the nitrogen pressure is also seen to affect the type and amount of transient mixed aluminium titanium oxides and the degree to which the initial TiO_2 is reduced before undergoing nitridation. Generally speaking, all observations can be rationalized with reference to equilibrium solid–gas phase diagrams computed from available thermochemical data.

Finally, since both the present and previous papers have been concerned with the behaviour of $1.5TiO_2 + 2AlN$ starting mixtures only, the effect of changing the AlN/TiO_2 ratio must be commented on. Both early work [4] and complementary experiments, not to be discussed further, have shown that no fundamentally new information arises from such variations of the AlN/TiO_2 contents. If the ratio is increased, residual AlN is detected in the final Al_2O_3–TiN composites. No aluminium oxynitride, by the way, was ever detected during the course of this work, consistent with the finding [5] that a minimum temperature of > 1900 K is required before AlN and Al_2O_3 react with each other. Conversely, reducing the AlN/TiO_2 ratio brings about the formation of fewer amounts of the mixed $Al_xTi_yO_5$ oxides with lower Al contents (small x) or even precludes the reduction of TiO_2 further than Ti_nO_{2n-1} where n depends on the starting AlN content. Whether such Ti_nO_{2n-1} is subsequently nitrided depends upon the effective nitrogen pressure as described in the present paper.

Acknowledgements

Thanks are due to Dr P. Möckli for invaluable help with the X-ray diffraction part of the work, and to the Swiss NSF for financial support under Contract No. 4.842.0.85.19.

Appendix: Calculated gas compositions in equilibrium with solid phases in Ti–O–N and Al–O–N systems at 1500 K

For the sake of simplicity, it is assumed that the Ti–Al–O–N system behaves as the conjunction of both the Al–O–N and Ti–O–N systems. This amounts to assuming that (i) no volatile species containing both elements Al and Ti needs be considered, and (ii) solid solutions have thermochemical properties equivalent to those of the pure solvent phases.

A1. The Ti–O–N system

A main concern of this work is with solid Ti_3O_5 and Ti_2O_3 phases and their vapourization. According to the literature Ti_3O_5 vaporizes either as [6]

$$Ti_3O_5(s) = 3TiO(g) + O_2(g)$$

or as [7]

$$Ti_3O_5(s) = TiO(g) + 2TiO_2(g)$$

and reactions in the gas phase are considered being limited to

$$TiO_2(g) = TiO(g) + \tfrac{1}{2}O_2(g)$$

$$TiO(g) = Ti(g) + \tfrac{1}{2}O_2(g)$$

In contrast, Ti_2O_3 is decomposed according to [8]

$$2Ti_2O_3(s) = Ti_3O_5(s) + TiO(g)$$

Although gaseous Ti_2O_3 and Ti_2O_4 have been reported for temperatures > 2200 K [9] we shall consider explicitly Ti(g), TiO(g) and TiO_2(g) only, and use JANAF Tables for the calculations. Finally, since TiN(g) is not taken into account by JANAF and no experimental reports were found of interactions between nitrogen and gaseous Ti oxides, we shall further assume these to take place according to

$$TiO(g) + \tfrac{1}{2}N_2(g) = TiN(s) + \tfrac{1}{2}O_2$$

The gas-phase composition in equilibrium with TiN and either Ti_3O_5 or Ti_2O_3 can then be calculated and Fig. A1 shows the results of such calculations at $T = 1500$ K as a function of p_{O_2}. It may be pointed out that the calculation was performed using the former of the above Ti_3O_5 vapourization reactions. When the latter is used instead, essentially similar results are obtained.

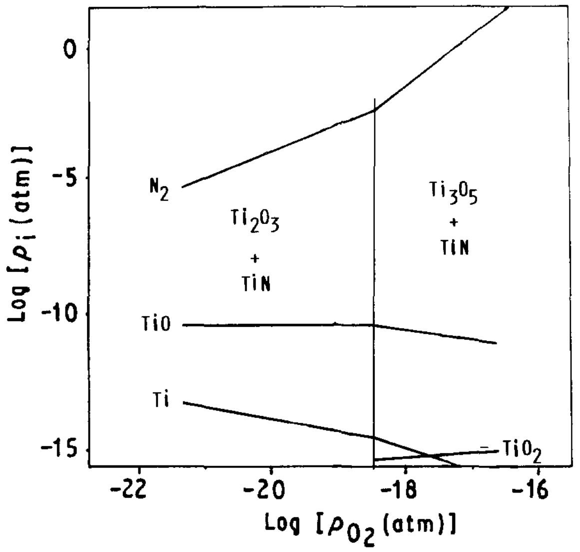

Figure A1 Equilibrium partial pressures at 1500 K in Ti–O–N system.

A2. The Al–O–N system

A number of volatile species, i.e. Al, AlO, Al_2O_2, Al_2O, AlO_2, have been noted in the Al–O system and are recorded in JANAF compilations. Despite a rather copious literature on the subject, the vapourization equation of condensed Al_2O_3 is still somewhat controversial. Two schemes have been advocated [10]

$$Al_2O_3(s) = 2Al(g) + \tfrac{3}{2}O_2$$

or

$$Al_2O_3(s) = Al(g) + AlO_2(g) + \tfrac{1}{2}O_2$$

Interactions within the gas phase in turn can be described by the following set of equations [11]:

$$Al(g) + \tfrac{1}{2}O_2 = AlO(g)$$

$$Al(g) + AlO(g) = Al_2O(g)$$

$$Al_2O(g) + AlO(g) = Al(g) + Al_2O_2(g)$$

$$Al(g) + AlO_2(g) = 2AlO(g)$$

On the other hand, AlN vapourizes congruently and, according to JANAF

$$AlN(s) = AlN(g)$$

$$AlN(g) = Al(g) + \tfrac{1}{2}N_2$$

or

$$AlN(g) + \tfrac{1}{2}O_2 = AlO(g) + \tfrac{1}{2}N_2$$

Fig. A2 shows similarly the results of equilibrium partial pressure calculations at $T = 1500$ K, versus p_{O_2}.

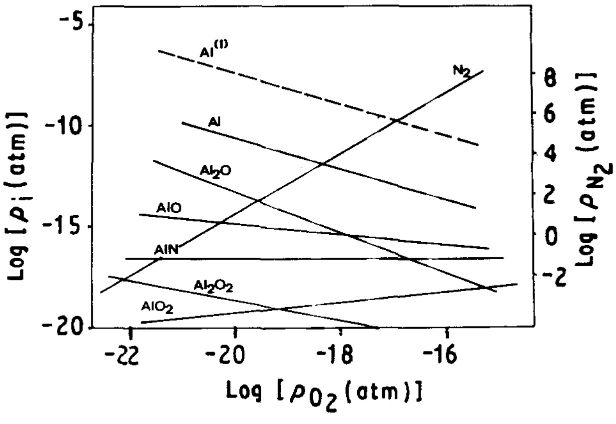

Figure A2 Equilibrium partial pressures at 1500 K in Al–O–N system.

Here again the former of the above Al_2O_3 vapourization equations has been assumed to hold. If the latter equation is used instead, still higher equilibrium Al and AlO pressures will arise. However, whichever of the AlN(g) decomposition schemes is assumed to dominate, it is seen not to play an important role in the results.

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Received 20 December 1990
and accepted 13 May 1991