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Combustion Synthesis of Aluminium Titanate

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Abstract

Initial interest in aluminium titanate was due to its low thermal expansion coefficient and high thermal shock resistance, but further research was soon discouraged following the discovery of the expansion anisotropy and the instability of the compound over a specific range of temperatures. The development of a suitable active precursor powder could provide a possible solution to the fabrication difficulties (microcracking and decomposition). The scarce available thermodynamic data for the formation of Al_2TiO_5 from its constituent oxides indicate that the reaction is endothermic and only possible at high temperature because of the titanate being entropy stabilised. The present work describes a straightforward combustion synthesis technique to prepare submicron Al_2TiO_5 powders, using the corresponding metal precursors-urea mixtures, at low temperature and short reaction times. A thermodynamic interpretation of the reaction is provided and the characteristics of the powder produced, like morphology, specific surface area and grain size, are discussed. The thermal behaviour of the combustion powder is compared with that of Al_2TiO_5 produced via the conventional ceramic solid state route. © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Initial interest in aluminium titanate, Al_2TiO_5, was due to its low thermal expansion coefficient (typically of the order of $1-2\times10^{-6}$ K^{-1}), but further research was soon discouraged following the discovery of the expansion anisotropy, leading to extensive microcracking during cooling, and the instability of the compound over the temperature range of $\sim800-1280°C$. Aluminium titanate

belongs to the pseudobrookite family of compounds with the general formula A_2BO_5, represented by the homologous Fe_2TiO_5. In the Al_2TiO_5 structure, each Al^{3+} or Ti^{4+} cation is surrounded by six oxygen ions forming distorted oxygen octahedra. These AlO_6 or TiO_6 octahedra form (001) oriented double chains weakly bonded by shared edges. Such structure is responsible for the strong thermal anisotropy, which creates a complicated system of localised internal stresses during cooling from the firing temperature. These stresses can, and frequently do, exceed the intrinsic fracture strength of the material, resulting in severe microcracking. This microcracking is responsible for the mechanical weakness of the ceramic and explains the quoted low thermal expansion coefficient. These microcracks also contribute to a low thermal conductivity and an excellent thermal shock resistance.

Various models were proposed[1] to relate grain size to microcracking phenomena observed in anisotropic materials, all of them agreeing in the fact that there is a critical grain size below which the energy available in the system is insufficient to create microcracks. That critical grain size is a material-related property and is inversely proportional to the square of the degree of thermal expansion anisotropy. Ohya et al.[2] applied the fundamentals of the theory proposed by Bradt et al.,[3] combining the internal stress and the energy criteria, directly to aluminium titanate and showed that no stress relaxation occurred below a sintering temperature of 1500°C. Based on this, they proposed that the critical grain size for aluminium titanate is not a unique value but varies inversely with the sintering temperature below 1500°C. Hence, lower sintering temperatures result in a larger critical grain size and less microcracking. In the sintered material, therefore, if the final grain size is kept below a critical value ($\sim1-4\,\mu m$), microcracking can be reduced and the mechanical strength greatly improved.[3,4]

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In the Al_2O_3–TiO_2 system, aluminium titanate is the only stable compound above 1280°C, up to its melting point. Below that temperature, however, Al_2TiO_5 decomposes to produce α-alumina and rutile. Fast firing studies[5] (i.e. high heating rates and sintering times as short as 1 min) showed that the titanate could already be detected at 1250°C but, at that temperature, increasing the sintering time led back to the decomposition, suggesting a metastable primary crystallisation. The small aluminium ion (ionic radius of 0·050 nm) is in a structural site of higher dimension, which is expected to affect the thermal stability of the structure. There is ongoing debate over the decomposition mechanisms upon cooling from synthesis and/or sintering temperature,[6] but experimental evidences suggest a nucleation and growth controlled process, affected by the characteristics of the initial powder and the processing variables (compaction pressure and sintering temperature and time). Consensus has it that the decomposition rate peaks at 1100°C and that residual alumina particles might act as preferred nucleation sites for the decomposition. Additives have been used, both as solid solutions (i.e. increasing the entropy, the decomposition temperature should fall to such values that the reaction is kinetically inhibited) and secondary phases (i.e. diffusion barriers), to counteract the thermal instability and simultaneously improve the mechanical strength.

The fabrication difficulties could find a possible solution if a suitable active precursor powder is developed. The scarce available thermodynamic data for the formation of Al_2TiO_5 from its constituent oxides[7] indicate that the reaction is endothermic and only possible at high temperature because the titanate is entropy stabilised, i.e. the major contribution for the ΔG^0 is the $T\Delta S^0$ term ($T = 1280$°C when $\Delta G^0 = 0$). This stabilisation has been attributed to the disordering of the cation network in pseudobrookites.[8] The work carried out so far has established that the formation of the titanate is a wholly solid state reaction involving a standard slow nucleation and rapid grain growth process controlled by diffusion, the apparent activation energy of the overall process being in the order of 700 kJ mol^{-1}.[9–11]

The most common powder synthesis route is still the solid state reaction method, in which fine powders of the individual component oxides are first mixed and then calcined at elevated temperatures. Sometimes repeated grinding and calcining steps might be required in order to achieve the desired phase. Even so, the resulting material may still contain secondary phases or unreacted components and it is difficult, with this method, to avoid contamination from grinding and obtain a compositionally homogeneous product. Furthermore, in the case of aluminium titanate, the starting powder grain size might already be above the sintered critical grain size necessary to avoid microcracking during cooling.

The use of wet chemical synthesis methods for aluminium titanate[12–14] is rather attractive, even if those methods usually are elaborated procedures. They present the possibility of producing high purity powders at low temperatures, with high sinterability, high surface area, well defined chemical compositions and homogeneous distribution of the elements. The temperature of formation of Al_2TiO_5, determined by DTA, was reported to be in the range 1360–1400°C, depending on the preparation route of the precursor mixture.

Still, it remains to be proven that these ultrafine powders will enable the production of sintered materials with a final grain size below the critical size, since grain growth seems to occur spontaneously as a consequence of the expansive formation of the titanate (theoretical density of $3·7 \times 10^3$ kg m^{-3}, as opposed to $4·1 \times 10^3$ kg m^{-3} expected for an equimolar mixture of Al_2O_3 and TiO_2). Densification studies, aimed at determining the prevalent mass transport mechanisms, are also complicated by this expansion, which opposes the sintering effect.

In recent years, combustion synthesis[15–18] has come up as a quick, straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated multicomponent oxide ceramic powders, without the intermediate decomposition and/or calcining steps. The method exploits an exothermic, usually very rapid and self-sustaining chemical reaction between the desired metal salts and a suitable organic fuel, which is ignited at a temperature much lower than the actual phase transformation temperature. Its key feature is that the heat required to drive the chemical reaction and accomplish the compound synthesis is provided by the reaction itself and not by an external source (the large amounts of gases formed can result in the appearance of a flame, which can reach temperatures in excess of 1000°C).

To produce a mixed oxide, a mixture containing the desired metal cations, preferably in the form of water soluble nitrates, and a fuel, like urea, can be used. By simple calcination, the metal nitrates can, of course, be decomposed into metal oxides upon heating to or above the phase transformation temperature. A constant external heat supply is necessary in this case, to maintain the system at the high temperature required to accomplish the appropriate phase transformation. Various other fuels, with different 'reducing power', have been used but, for most purposes, urea has proven[17,18] to be

the most convenient fuel to use: it is readily available commercially, is cheap and generates the highest temperature, although fuel-rich mixtures might produce prematurely sintered particle agglomerates. The basis of the combustion synthesis technique comes from the thermochemical concepts used in the field of propellants and explosives, and its extrapolation to the combustion synthesis of ceramic oxides and thermodynamic interpretation is extensively discussed elsewhere.[17]

The work that follows describes the powder synthesis of aluminium titanate by combustion reaction of redox mixtures of the corresponding metal precursors with urea and compares its characteristics with those of powders with the same composition prepared from the individual oxides by the solid state route.

2 Experimental Procedure

Aluminium titanate was synthesized by combustion reaction using Merck $Al(NO_3)_3.9H_2O$ and Aldrich liquid $Ti[O.CH(CH_3)_2]_4$, as cation precursors, and Labsynth r.g. urea $CO(NH_2)_2$ as fuel. Reagex p.a. $NH_4.NO_3$ was used as combustion aid, as described later. Handling of the liquid propoxide was done with a syringe, after converting the required number of moles to volume using the molecular weight and density given by the supplier. The appropriate amounts of the reactants (batches were calculated on a basis of 6 ml of titanium isopropoxide), with a little added water, were first melted in a wide-mouth vitreous silica basin (~200 cm^3) by rapid heating up to ~300°C on a hot-plate inside a fume-cupboard, under ventilation. Soon after the liquid thickened and began frothing, the basin was transferred to a muffle furnace preheated at 500°C where ignition took place. The reaction lasted for less than 1 min and produced a dry, white and very fragile foam, that easily crumbled into powder. This foam was then lightly ground in the silica basin with a porcelain pestle and the powder sieved through 325 mesh.

The BET specific surface area of the as-prepared combustion reaction product was determined in N_2/He with a Quantasorb Quanta-Chrome apparatus. The corresponding particle size distribution was obtained with a Malvern Zetasizer 4 apparatus in diluted aqueous suspensions, after ultrasonic deagglomeration.

The as-prepared combustion reaction product was uniaxially pressed at ~500 MPa (~60% relative green density) into cylindrical pellets, which were then sintered in air at 1500°C (10°C min^{-1}) for 2 h, in a SuperKanthal electric furnace. Relative green and sintered densities were calculated geometrically

(diameter and thickness measurements were carried out with a micrometer) as a qualitative assessment of the powder compaction and sintering behaviour. The theoretical density of Al_2TiO_5 was assumed to be 3.7×10^3 kg m^{-3}.

The as-prepared combustion reaction product, powders calcined at various temperatures and selected sintered samples, after hand grinding, were characterised by X-ray diffraction (Cukα/Ni Siemens Kristalloflex D5000 diffractometer, with a scanning rate of 2° 2θ min^{-1}, in a 2θ range of 15 to 45°) and Scanning Electron Microscopy (W filament Leica Cambridge StereoScan 440, after Au coating) with semi-quantitative micro-analysis (Oxford EDS probe).

Differential Scanning Calorimetry (DSC) studies were carried out in air on green pellets in a Netzsch DSC 404 apparatus from ambient temperature up to 1400°C, with a heating rate of 20°C min^{-1}. Fracture surfaces of selected sintered samples were also observed in the SEM and chemical compositions were obtained as semi-quantitative EDS spectra and element maps.

3 Results and Discussion

3.1 Combustion reactions

From published thermodynamic data such as those listed in Table 1, the enthalpy change involved in the various chemical reactions can be calculated. The combustion reaction of urea (total valencies $+6$), described by equation R1 in Table 2, is exothermic and should supply the heat needed for the synthesis reaction. To prepare the aluminium titanate by the combustion route crystalline

Table 1. Relevant thermodynamic data[19][21]

Compound[a]	ΔH_f° (25°C) (kcal mol^{-1})	Cp (cal mol^{-1}K^{-1})
$Al(NO_3)_3.9H_2O_{(c)}$	-897.57	—
$Ti[O.CH.(CH_3)_2]_{4(l)}$	-145.32^b	—
$CO(NH_2)_{2(c)}$	-79.71	22.26
$Al_2TiO_{5(c)}$	-620.23^c	—
$Ti(OH)_{4(c)}$	-431.3^b	—
$CH.(CH_3)_2.OH_{(g)}$	-60.93	20.44
$CH.(CH_3)_2.OH_{(l)}$	-72.27	—
$TiO_{2(c)}$ (rutile)	-225.8	13.15
$Al_2O_{3(c)}$ (corundum)	-400.4	$2.97 + 0.0773$ T^{d,e}
$NH_4.NO_{3(c)}$	-87.46	33.33
$NH_{3(g)}$	-10.98	8.39
$H_2O_{(g)}$	-57.796	$7.20 + 0.00360$ T^d
$CO_{2(g)}$	-94.051	$10.34 + 0.00274$ T^d
$N_{2(g)}$	0	$6.50 + 0.00100$ T^d
$O_{2(g)}$	0	$5.92 + 0.00367$ T^{d,e}

^{a}(c) = crystalline, (g) = gas, (l) = liquid.
^{b}Calculated from bond energies.[21]
^{c}Calculated from Ref. 7.
^{d}T is absolute temperature.
^{e}Calculated from discrete values.

Table 2. Equations describing the various chemical reactions that might be involved in the combustion synthesis

Reaction	Describing equation	$\Delta H°$ (25°C, kcal)[a]
R1	$CO(NH_2)_{2(c)} + 1·5\ O_{2(g)} \Rightarrow CO_{2(g)} + 2H_2O_{(g)} + N_{2(g)}$	$-129·9$
R2	$2\ Al(NO_3)_3.9H_2O_{(c)} \Rightarrow Al_2O_{3(c)} + 18\ H_2O_{(g)} + 3\ N_{2(g)} + 7·5\ O_{2(g)}$	$354·5$
R3	$Ti[O.CH.(CH_3)_2]_{4(1)} + 18\ O_{2(g)} \Rightarrow TiO_{2(c)} + 12\ CO_{2(g)} + 14\ H_2O_{(g)}$	$-2018·2$
R4	$Al_2O_{3(c)} + TiO_{2(c)} \Rightarrow Al_2O_3.TiO_{2(c)}$	$5·97^b$
RS1	$2\ Al(NO_3)_3.9H_2O_{(c)} + Ti[O.CH.(CH_3)_2]_{4(1)} + 10·5\ O_{2(g)} \Rightarrow$ $Al_2O_3.TiO_{2(c)} + 32\ H_2O_{(g)} + 3\ N_{2(g)} + 12\ CO_{2(g)}$	$-1657·8$
RS2	$2\ Al(NO_3)_3.9H_2O_{(c)} + TiO_{2(c)} \Rightarrow Al_2O_3.TiO_{2(c)} + 18\ H_2O_{(g)} + 3\ N_{2(g)} + 7·5\ O_{2(g)}$	$360·4$
RT1	$2\ Al(NO_3)_3.9H_2O_{(c)} + TiO_{2(c)} + m\ CO(NH_2)_{2(c)} \Rightarrow Al_2O_3.TiO_{2(c)} +$ $(18 + 2m)H_2O_{(g)} + (3 + m)\ N_{2(g)} + (7·5 - 1·5m)O_{2(g)} + m\ CO_{2(g)}$	$360·4 +$ $m(-129·9)$
R5	$Ti[O.CH.(CH_3)_2]_{4(1)} + 4\ H_2O_{(g)} \Rightarrow Ti(OH)_{4(c)} + 4\ CH.(CH_3)_2.OH_{(g)}$	$-332·5$
R6	$Ti(OH)_{4(c)} \Rightarrow TiO_{2(c)} + 2\ H_2O_{(g)}$	$89·9$
RS3	$2\ Al(NO_3)_3.9H_2O_{(c)} + Ti(OH)_{4(c)} \Rightarrow Al_2O_3.TiO_{2(c)} + 20\ H_2O_{(g)} + 3\ N_{2(g)} + 7·5\ O_{2(g)}$	$450·3$
RT2	$2\ Al(NO_3)_3.9H_2O_{(c)} + Ti(OH)_{4(c)} + mCO(NH_2)_{2(c)} \Rightarrow Al_2O_3.TiO_{2(c)}$ $+ (20 + 2m)\ H_2O_{(g)} + (3 + m)\ N_{2(g)} + (7·5 - 1·5m)\ O_{2(g)} + m\ CO_{2(g)}$	$450·3 +$ $m(-129·9)$
R7	$NH_4.NO_{3(c)} \Rightarrow NH_{3(g)} + 0·5\ H_2O_{(g)} + 0·5\ N_{2(g)} + 1·25\ O_{2(g)}$	$47·6$
RQ1	$NH_4NO_{3(c)} + nCO(NH_2)_{2(c)} \Rightarrow NH_{3(g)} + nCO_{2(g)} + (2n + 0·5)\ H_2O_{(g)}$ $+ (n + 0·5)\ N_{2(g)} + (1·25 - 1·5m)O_{2(g)}$	$47·6 +$ $n(-129·9)$

[a]Calculated from thermodynamic data listed in Table 1.
[b]From Ref. 7.

$Al(NO_3)_3.9H_2O$ can be used as Al source (total valencies -15). The individual reaction of the precursor nitrate, leading to the corresponding oxide, is listed in Table 2 as reaction R2.

A suitable precursor for Ti metal is more difficult to find. One possibility is an alkoxide like the liquid isopropoxide, $Ti[O.CH.(CH_3)_2]_4$ (total valencies $+72$). The use of a compound such as the propoxide is expected to introduce some changes in the redox reaction, given that its positive total valencies suggest fuel characteristics. In fact, the combustion reaction of $Ti[O.CH.(CH_3)_2]_4$ (reaction R3, Table 2) is highly exothermic and generates a large amount of gases, although the propoxide has low burning velocity and flame temperature. Still, from a thermodynamic point of view, the overall synthesis reaction (reaction $RS1 = R2 + R3 + R4$, Table 2) could be carried out on its own, fed by the heat of combustion of the propoxide. In practice, though, things do not happen this way and, without urea, the precursor mixture does not ignite and the titanate synthesis is not accomplished.

Direct use of the propellant chemistry criterion[1] with the metal precursors in a 2:1 molar proportion, to determine the urea needed to balance the total oxidising and reducing valencies in the mixture, leads to:

$$2(-15) + (+72) + n(+6) = 0$$

and the stoichiometric composition of the redox mixture, to release the maximum energy for the reaction, would demand that $n = -7$ mol of urea were used. This means that the mixture already contains excess fuel (in terms of 'reducing power' the required mole of propoxide is equivalent to

$72/6 = 12$ mol of urea). In other words, the stoichiometric urea requirements for the reaction are just those needed for the combustion synthesis involving the aluminium nitrate alone:

$$2(-15) + n(+6) = 0 \text{ or } n = 5·0$$

In this case, one might assume that the combustion of the propoxide will not contribute to the heat necessary for the titanate synthesis. Simple calcination of the propoxide, carried out in an open environment, will produce TiO_2 and the gases evolved will carry away the heat generated. With this assumption, instead of the synthesis reaction RS1, the actual reaction would be described as reaction $RS2 = R2 + R4$ (Table 2), which is endothermic and, therefore, requires the use of urea. The overall synthesis reaction would then be reaction $RT1 = RS2 + mR1$ (Table 2). For the Al_2TiO_5 synthesis reaction RT1 to occur at 25°C, on the basis of enthalpy change solely, $\Delta H_{RT1}° = 0 = +360·4 + m(-129·9)$ and only $m = 2·77$ mol of urea would be needed.

These 2·77 mol of urea satisfy the enthalpy requirement for complete decomposition at 25°C and release of all the corresponding gases, as predicted by reaction RT1 (i.e. $23·54\ H_2O_{(g)} + 5·77$ $N_{2(g)} + 3·35\ O_{2(g)} + 2·77\ CO_{2(g)}$). However, that temperature is not enough to promote the titanate synthesis and the single oxides (i.e. Al_2O_3 and TiO_2) will remain as reaction products. The combustion of the extra 2·23 moles of urea specified by the propellant chemistry calculations (i.e. $5 - 2·77 = 2·23$ mol), will consume all the released oxygen and the heat generated will be absorbed by the corresponding gases (i.e. $4·46\ H_2O_{(g)} + 2·23$

$N_{2(g)} + 2 \cdot 23\ CO_{2(g)}$), the remainder of those already present and the single oxides, raising their temperature. Using the relevant heat capacities listed in Table 1 and the ΔH_{R1} in Table 2, the temperature reached by all the final products would be $\sim 617°C$. This flame temperature is obviously not enough to promote the titanate synthesis.

Previous work on combustion synthesis reactions involving alkoxides as metal precursors[18] suggests that the most likely alternative to the independent combustion of the liquid propoxide, is its hydrolysis. This compound is frequently used in sol–gel processes which require that its strong tendency to hydrolysis by ambient moisture is inhibited. The hydrolysis reaction (reaction R5, Table 2) should produce $Ti(OH)_4$ and propanol which, due to its low boiling point ($97 \cdot 3°C$), will leave the system even before the nitrate decomposes. With this assumption, only the hydroxide will participate in the synthesis and, instead of the synthesis reaction RS1, the actual reaction would be reaction RS3 = R2 + R6 + R4 (Table 2), which is also endothermic and requires the use of urea. The overall synthesis reaction would then be reaction RT2 = RS3 + mR1 (Table 2). For the titanate synthesis reaction RT2 to occur at 25°C, on the basis of enthalpy change solely, $\Delta H_{RT2}° = 0 = +450 \cdot 3 + m(-129 \cdot 9)$ and only $m = 3 \cdot 47$ mol of urea would be needed.

As before, these $3 \cdot 47$ mol of urea represent the minimum enthalpy requirement for the decomposition reactions to be completed at 25°C and all the corresponding gases released (i.e. $26 \cdot 94\ H_2O_{(g)} + 6 \cdot 47\ N_{2(g)} + 2 \cdot 30\ O_{2(g)} + 3 \cdot 47\ CO_{2(g)}$), as predicted by reaction RT2. Again, that temperature is not enough to promote the synthesis of the titanate and the single oxides will remain as reaction products. The combustion of the extra $1 \cdot 53$ moles of urea specified by the propellant chemistry calculations ($5 - 3 \cdot 47 = 1 \cdot 53$ mol), will consume all the oxygen released and the heat generated will be absorbed by the corresponding gases (i.e. $3 \cdot 06\ H_2O_{(g)} + 1 \cdot 53\ N_{2(g)} + 1 \cdot 53\ CO_{2(g)}$), the remainder of those already present and the single oxides, raising their temperature. Using the relevant heat capacities listed in Table 1 and the ΔH_{R1}, in Table 2, the temperature reached by all the final products will be $\sim 437°C$. As before, this temperature is definitely insufficient to accomplish the titanate synthesis.

Thus, whether the propoxide burns or hydrolyses before the synthesis, the previous thermodynamic calculations show that the temperature reached will not be high enough to promote the compound synthesis. The combustion reaction carried out with the reactants in the molar proportions specified by the propellant chemistry (i.e. 2:1:5) occurred with easy development of a strong but not so bright flame and led to the formation of a fluffy white dry powder. However, the X-ray diffraction pattern of as-prepared powders showed no crystalline phases (Fig. 1). Calcining at 1150°C for 105 min led to the crystallisation of only rutile and α-alumina (Fig. 1). Apparently, the rather high activation energy of the titanate formation process is not overcome during the combustion reaction. Therefore, the use of additional fuel and/or oxidiser will be required if the compound synthesis is to be accomplished during combustion.

3.2 Combustion with excess fuel

The literature reports that the temperature of formation of Al_2TiO_5, determined by DTA, is in the range 1360–1400°C, depending on the preparation route of the precursor mixture.[12–14] The theoretical temperature expected for the combustion reactions, both for the RT1 and RT2 mechanisms, calculated thermodynamically as described above using different excess fuel contents, is given in Table 3. According to the values in the Table, only a 200% excess urea would suffice to accomplish the titanate synthesis. Different batches were prepared with the various fuel contents, i.e. 2:1:10 (100% excess), 2:1:12·5 (150% excess) and 2:1:15 (200% excess), keeping the desired molar proportion of the metal precursors constant. The combustion reactions lasted visibly longer but without flame, producing a foam that shrunk like a burning polymer. This fact is an indication of premature sintering of the powder particles and cautions against the use of fuel-rich mixtures. However, the X-ray diffraction patterns of the three as prepared powders showed no crystalline phases (Fig. 1).
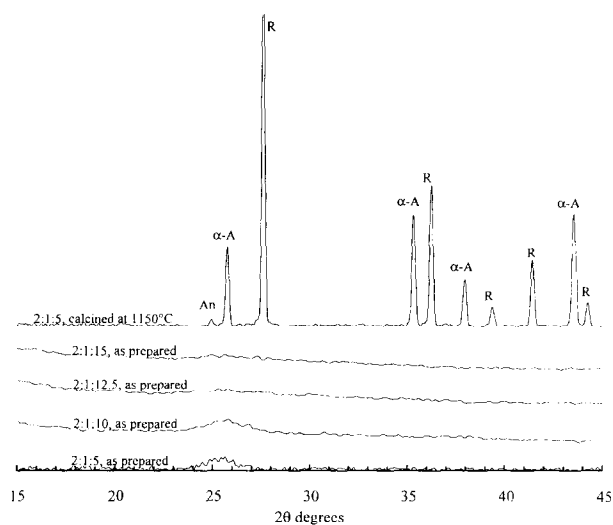

Fig. 1. X-ray diffraction patterns of the as prepared powders, as a function of the urea content of the redox mixture, and the 2:1:5 powder after calcining at 1150°C α-A = (α-alumina, R = rutile, An = anatase).

Table 3. Theoretical temperatures reached by the combustion reactions, as a function of the molar proportions of the reactants in the redox mixtures, for the RT1 and RT2 mechanisms (see Table 2)

| Molar proportions $Al(NO_3)_3.9H_2O$: $Ti[O.CH.(CH_3)_2]_4$ | 2:1 | Theoretical temperature (°C) | |
		RT1	RT2
$CO(NH_2)_2$	5	617	437
(100% excess)	10	1108	1040
(150% excess)	12·5	1256	1202
(200% excess)	15	1368	1324

3.3 Combustion with additional oxidiser

Given the unsuccessful stoichiometric combustion synthesis of the titanate, already predicted by the thermodynamic calculations described earlier, as well as the combustion with excess fuel, the effect of an additional oxidiser was investigated. For this purpose, and in order to keep the metal cation proportion constant, $NH_4.NO_3$ was used.

The combustion reaction of the ammonium nitrate (total valencies -2) can be described by reaction RQ1 $= R7 + nR1$, in Table 2. The enthalpy balance for the reaction to occur at 25°C, demands the use of 0·37 mol of urea per mole of nitrate. This urea requirement is essentially the same as that specified by the propellant chemistry criterion for the maximum energy release, which is $n = 0·33$. Thus, the addition of $NH_4.NO_3$ and the corresponding urea is not expected to alter the theoretical temperature but will produce extra combustion gases, having the effect of expanding the foam structure beyond that obtained with the metal precursors alone and eventually increasing the corresponding surface area. Most importantly, having the ammonium nitrate igniting inside the precursors mixture might boost the overall reaction to overcome the high activation energy barrier involved in the titanate synthesis. The $NH_4.NO_3$ is therefore expected to act as a combustion aid.

Following this reasoning, new batches were prepared keeping the desired molar proportions of the metal precursors and adjusting the urea content to that of the added ammonium nitrate. Mixtures were prepared with $Al(NO_3)_3.9H_2O$, $Ti[O.CH.(CH_3)_2]_4$, $NH_4.NO_3$ and $CO(NH_2)_2$ in the molar proportions of, respectively, 2:1:1:5·33, 2:1:2:5·67 and 2:1:4:6·33. The combustion reactions lasted as long as those without the ammonium nitrate but, after ignition, the foam rose higher and reached a bright incandescence. Figure 2 shows the X-ray diffraction patterns of the three as-prepared powders. All three show the distinctive aluminium titanate peaks and the presence of some anatase. No α-alumina was found and traces of rutile were detected in the 2:1:4:6·33 powder. The presence of rutile, the high temperature crystalline form of
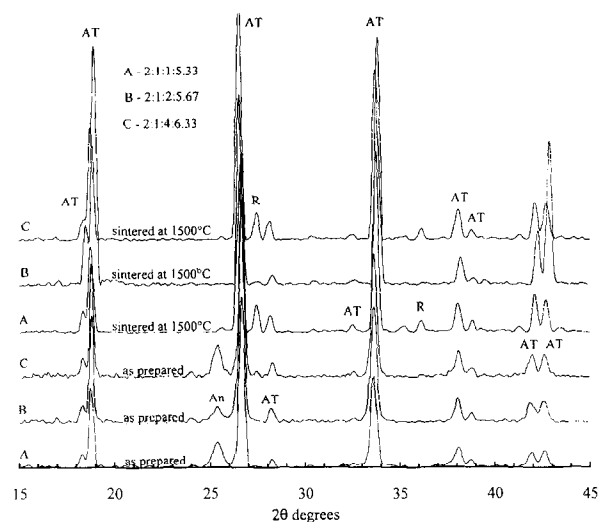

Fig. 2. X-ray diffraction patterns of the as-prepared powders, as a function of the $NH_4.NO_3$ content of the redox mixture, and after sintering at 1500°C (AT = titanate, R = rutile, An = anatase).

TiO_2, in this powder, as opposed to the presence of anatase in the others, suggests that the maximum benefit from the combustion aid has been achieved and that some of the extra energy is being used to promote the crystallisation of the individual oxides instead of the titanate. The simultaneous absence of crystalline alumina indicates that either the combustion was not fully efficient, in which case the missing alumina must be amorphous, or an alumina-rich titanate solid solution was formed. To rule out possible stoichiometry inaccuracies introduced by the reactants, the conversion degree of their individual reactions was also investigated.

The combustion reaction of $Al(NO_3)_3.9H_2O$ with urea was monitored in the molar proportion of 2:5, as required by propellant chemistry. The combustion produced a pop-corn like dry foam that proved to be crystalline alumina, with a 13·4% yield, i.e. comparable to the 13·6% theoretically predicted by reaction R2 (Table 2).

As for $Ti[O.CH(CH_3)_2]_4$, both the hydrolysis and the calcination were monitored. The hydrolysis (reaction R5 in Table 2) was carried out in a shallow dish by simple overnight exposure of the propoxide to ambient moisture, which reduced it to a white powder, followed by drying at 110°C for 5 h. The corresponding yield was found to be 40·2%, comparable to the theoretical value of 40·6%. The hydrolysis produced a completely amorphous powder that was then calcined at 900°C (10°C min^{-1}) for 1 h. After calcination, anatase and rutile were detected by X-ray diffraction, with a 69·0% yield, so fitting the 68·7% theoretical value (reaction R6 in Table 2).

Therefore, both reactants contribute as expected to the titanate formation and the products of the aided combustion reactions were further

investigated. The three combustion-aided as-prepared powders were compacted into pellets to ~60% relative green density and sintered at 1500°C (10°C min^{-1}) for 2 h. The sintered pellets were reground and the corresponding X-ray diffraction patterns are also shown in Fig. 2. While the 2:1:2:5·67 powder presented only the aluminium titanate peaks, both the other two powders show rutile and corundum peaks, indicating that the as-prepared powder characteristics play an important role during sintering and that there is an optimum content of combustion aid, below or above which its presence is detrimental to the efficient synthesis of the titanate. In all cases, the sintered density was found to be higher than ~70%, with a likely tendency to peak for the 2:1:2:5·67 sample (~80%). Thus, the best reaction, i.e. that which showed the smallest anatase peak in the as-prepared powder diffractogram and led to aluminium titanate alone after sintering, seems to be the one with the reactants in the 2:1:2:5·67 molar proportion. This composition is designated by stoichiometric in what follows.

Figure 3 illustrates the typical morphology of the combustion powders. The shattered glass look masks what must be the submicron size crystals clearly detected by the X-ray diffraction. The higher magnification micrograph in Fig. 3 shows the thinness of the shattered pieces of the solid foam that results from the combustion reaction, which largely determines the crystallite size in the powder particles. The BET specific surface area of the powder was determined to be ~11 m^2 g^{-1} and the corresponding particle size distribution is shown in Fig. 4. The average particle size was found to be 927 nm, all particles being smaller than
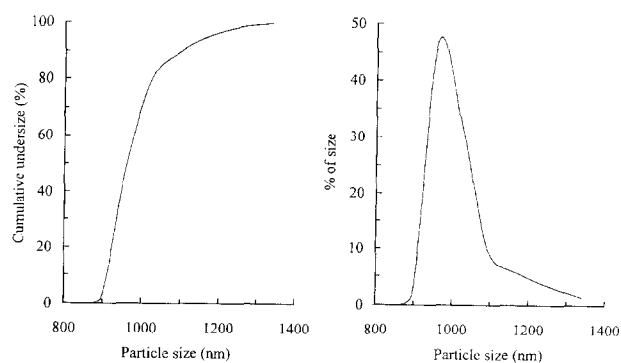

Fig. 4. Particle size distribution in the as-prepared combustion powders.

1·3 μm. The dot map in Fig. 3 illustrates the very homogeneous distribution of the elements. The EDS analysis, carried out on a fracture surface of the sintered sample, revealed an Al:Ti atomic proportion of ~2·5:1, which supports the possible formation of an alumina-rich titanate solid solution during the combustion synthesis. No individual alumina or titania grains were found in the microstructure.

3.4 Effect of excess alumina

Although the Al:Ti proportions used in the titanate combustion synthesis were accurate and as prescribed by the reactions in Table 2, the EDS analysis suggests the incorporation of excess alumina in the titanate, corroborated by the presence of anatase peaks, albeit small, in the diffractogram of the as prepared stoichiometric powder. New batches were prepared with different excess contents of the alumina precursor, namely 2·314:1:2:6·452 and 2·674:1:2:7·352, and compared with the stoichiometric composition (2:1:2:5·67). The corresponding
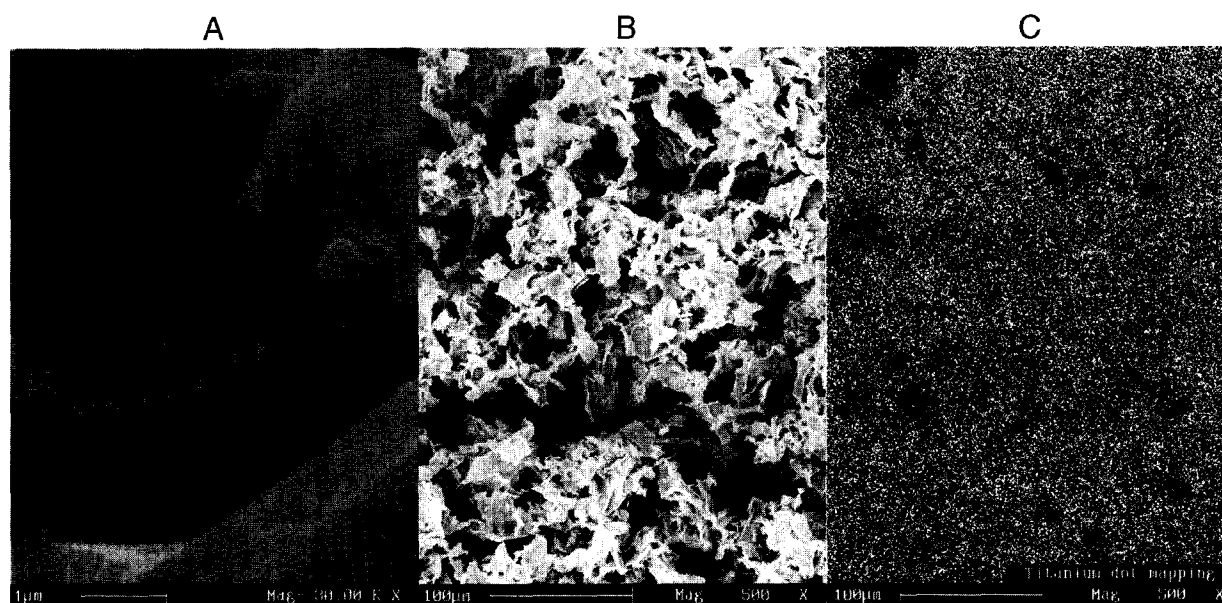

Fig. 3. Typical morphology (A and B) and element mapping (C) of the as-prepared combustion powders, as observed in the SEM.

as-prepared powder X-ray diffraction patterns are shown in Fig. 5. Crystalline alumina is present in none of them, anatase is practically absent in the 2·314:1:2:6·452 composition but can still be detected in very small amounts in the other compositions. The Al:Ti atomic proportion determined by EDS in the titanate grains in the 2·314:1:2:6·452 composition was found to be ~3·9:1.

Calcining these powders at 950°C (10°C min^{-1}) for 2 h led to the partial decomposition of the titanate formed during the combustion into rutile and corundum, in an extent that increases with the aluminium content in the mixture (Fig. 5). The X-ray diffraction patterns of pellets sintered at 1500°C (10°C min^{-1}) for 2 h, also presented in Fig. 5, show the corundum peaks in the excess alumina compositions and the richest alumina powder also presents rutile peaks, a sign of the alumina-induced decomposition of the titanate, as reported in the literature.

3.5 Thermal behaviour

Most studies on the sintering mechanisms of the aluminium titanate are concerned with reaction-sintering from the individual oxides. The powders produced in the combustion synthesis of the titanate are especially adequate for such studies, given that they already have the desired composition, are easy to produce and have very fine particle size. However, foreknowledge of the thermal stability of these powders is desirable.

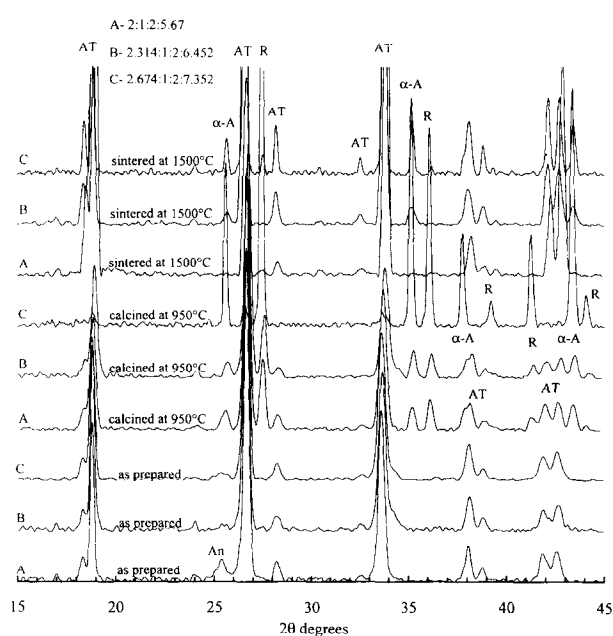The thermal behaviour of titanate powders produced by combustion synthesis was investigated by DSC on green pellets and the resulting curve is shown in Fig. 6 (marked as 'combustion, as-prepared'). After the initial stabilisation period, the DSC curve of the as-prepared powder shows the smooth decline characteristic of a grain growth process. The exothermic peak at 1176°C can only be attributed to the decomposition of the titanate formed during the combustion. This value is in agreement with that reported in the literature for the temperature at which the decomposition rate is highest. The titanate re-forms at 1338°C (endothermic peak in the DSC curve), which is also in agreement with the literature. The presence of a unique and well defined endothermic peak suggests a fast formation reaction, with a spread out nucleation process instead of the localised nucleation in preferred sites, common in fine powders sintered at lower temperatures, mentioned in literature.

To confirm the decomposition of the titanate during heating to the sintering temperature, combustion powders calcined at 950°C for 2 h, which led to nearly complete decomposition into rutile and corundum (Fig. 5), were uniaxially pressed into a pellet and a new DSC curve was obtained (Fig. 6, 'combustion, after decomposition'). This is the curve of an intimate mixture of submicron oxides and shows as sole accident the endothermic peak of the titanate formation, at the same temperature as before.

Figure 6 also shows, just for comparison, the DSC curve (marked as 'mixture of oxides, raw') obtained with a conventional raw ball-milled

Fig. 5. X-ray diffraction patterns of the as-prepared powders, as a function of the Al(NO₃)₃.9H₂O content of the redox mixture, and after calcining at 950°C and sintering at 1500°C (α-A = α-alumina, AT = titanate, R = rutile, An = anatase).
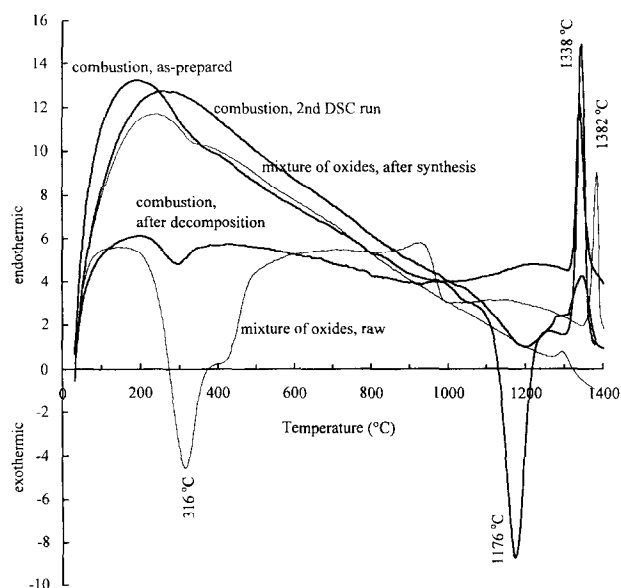

Fig. 6. DSC curves obtained with green compacts of titanate powders ('combustion, as-prepared' and 'mixture of oxides, after synthesis') and mixtures of precursor oxides ('combustion, after decomposition' and 'mixture of oxides, raw'), and with a pre-sintered compact ('combustion, 2nd DSC run'). See text for details.

mixture of reagent grade Al and Ti oxides, pre-
pared in a parallel study. The DSC pellet was
pressed at ~150 MPa in order to obtain a green
density of ~60%, as in the combustion powder
compact. The initial exothermic peaks correspond
to the burn-out of binders and compaction aids.
The step change near 1000°C is usually associated
with a change in specific heat and the inversion of
anatase to rutile. Finally, the endothermic peak of
the titanate formation occurs at 1382°C. According
to the literature, this temperature, higher than that
observed with the as prepared combustion powder,
is probably due to a larger initial particle size in the
mixture of oxides powder. After sintering at
1500°C (10°C min^{-1}) for 2 h, to accomplish the
titanate synthesis by the ceramic solid state route
(residual rutile and corundum peaks could still be
found in the corresponding X-ray diffraction pat-
tern), the sample was hand ground to powder
again, compacted into a pellet and used to obtain
the DSC curve of the mixture of oxides titanate,
also shown in Fig. 6 ('mixture of oxides, after sin-
tering'). The curve path follows closely that of the
combustion titanate, but no decomposition peak is
observed. The observed grain growth at low tem-
peratures in both curves must be occurring within
pre-sintered powder agglomerates, which might
lead to abnormal grain growth. The small titanate
formation peak observed for the mixture of oxides
titanate, nearer that in the combustion curve than
the one in the raw mixture of oxides, might just be
the final reaction between the residual oxides

rather than titanate re-formation following some
decomposition during heating up. The absence of a
decomposition peak could be explained by a tigh-
ter sintered microstructure as the result of the
previous sintering step in the presence of con-
taminants introduced by the milling step, which
would act as sintering aids.

To throw light into this behaviour, the combus-
tion DSC pellet already submitted to a so to say
fast-firing treatment during the first DSC run, was
used to obtain a second-run DSC curve, also
shown in Fig. 6 ('combustion, 2nd DSC run'). In
the second run the decomposition degree was
lower, hence, the titanate formation peak is smal-
ler. These results suggest that the physical con-
straint of the titanate grains within the sintered
microstructure has some inhibiting effect on its
decomposition during heating up.

As an illustration and for comparison, the sin-
tered microstructures (1500°C, 2 h) of the as-pre-
pared combustion powder and the mixture of
oxides powder are shown in Fig. 7. The key differ-
ence between the two fracture surfaces is the grain
morphology, round and smooth with transgranular
micro cracks in the mixture of oxides sample, sug-
gesting a grain growth process in the presence of
some liquid phase, and sharp-edged and more het-
erogeneous in the combustion sample, as if each
original foam flake had sintered on its own, leading
to some abnormal grain growth. In this sample,
hardly any microcracks were found and, when
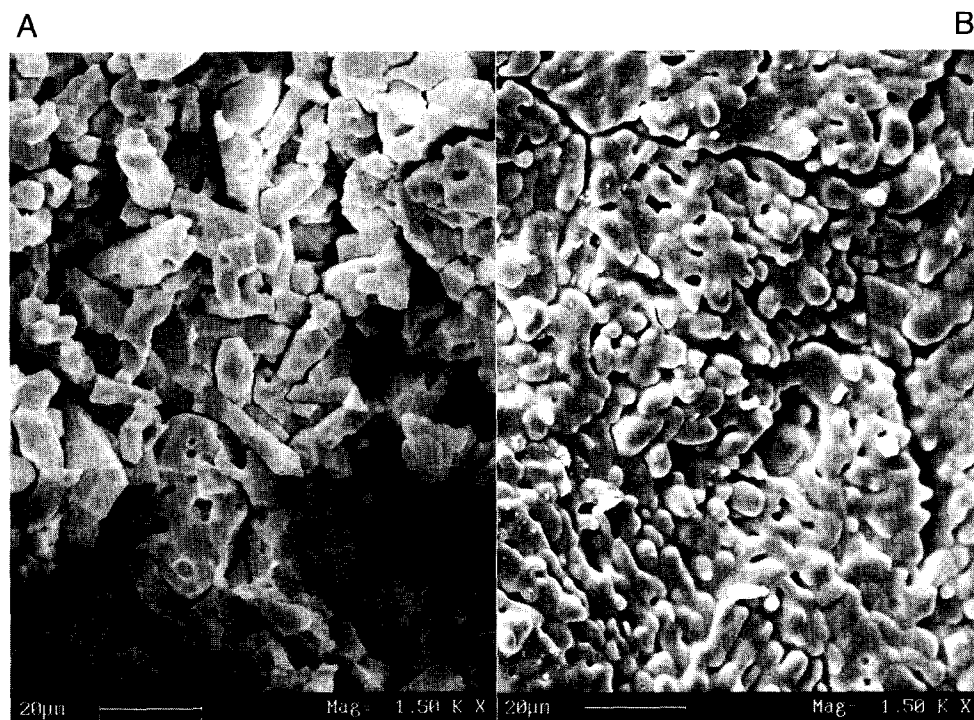present, they run intergranularly. The tighter

Fig. 7. Typical morphology of fracture surfaces of sintered samples, as observed in the SEM: (A) produced by combustion reaction and (B) produced by the solid state ceramic route.

microstructure observed in the mixture of oxides sample supports the hypothesis of a larger inhibition effect on the decomposition of the titanate indicated by the DSC curves. The Al:Ti atomic proportion in the titanate grains of the sintered mixture of oxides sample was also determined by EDS and found to be ~3·7:1. This surprisingly high value suggests that not only the formation of the titanate probably occurs via an intermediate alumina-rich solid solution but also that the synthesis reaction is easier when carried out by combustion.

4 Conclusions

The present work shows that the combustion synthesis technique is reliable and can be adapted to successfully produce pure, crystalline aluminium titanate, with good compositional control of the powders produced. With the reactants in the stoichiometric molar proportions predicted by the propellant chemistry, the reaction occurs but the titanate synthesis is not accomplished and will eventually take place only at elevated temperature from the non-crystalline individual oxides produced in the combustion. In this case, the combustion synthesis, although simpler and less expensive, is no better than the other alternative powder synthesis techniques. However, the unsuccessful combustion synthesis of unaided mixtures validated the assumptions made in the theoretical calculation of the maximum temperature reached in the stoichiometric reaction.

The results obtained show that, given the high activation energy of the titanate formation, combustion synthesis of Al_2TiO_3 is effective when a combustion aid is introduced, requiring no further exposure to temperature. Combustion synthesis offers then as advantages the simplicity of experimental set-up, the very short period mediating between the preparation of the reactants and the availability of the final product, the savings in external energy consumption and the equally important potential of simplifying the processing prior to forming.

The DSC study carried out showed that below the titanate stability temperature, the decomposition reaction is dominant and occurs upon heating to the sintering temperature. The intimate homogeneity of the combustion powder and very fine crystallite size might be responsible for the lower phase formation temperature observed and the very clean sintered microstructure. The microstructure constraint after sintering was shown to inhibit the heating-up thermal decomposition of the titanate. The chemical and morphological homogeneity of such powders is expected to give rise to highly dense fine-grained and single-phase polycrystals, thus reducing the tendency to microcracking and decomposition during fabrication. A systematic sintering/densification study is needed to clarify the apparent non-densifying behaviour of the combustion titanate and the presumed liquid phase assisted reaction sintering of the mixture of oxides.

A qualitative comment can be made regarding the EDS results, which suggest the existence of a solid solution range extending into the alumina-rich side of the stoichiometric Al_2TiO_3.

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