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Technical note

Combustion of the “Ti–TiO_2” and “Ti–Al” powdery mixtures in air

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Abstract

The combustion synthesis in “Ti–TiO_2” and “Ti–Al” powdery mixtures in air under atmospheric pressure has been studied. The results of X-ray diffraction analysis showed TiN and AlN as prevalent phases in the combustion products. Hence, the deep interaction with atmospheric nitrogen during metals combustion in air occurs. The mechanism of TiN and AlN formation instead of thermodynamically stable TiO_2 and Al_2O_3 formation by burning in air is proposed on the basis of XRD and SEM data.

Keywords: Powders-gas phase reaction; X-ray methods; Chemical properties; Nitrides; Refractories

1. Introduction

Nitrides, especially those of transition metals, have received increasing attention in the recent time because of their unique ceramic properties. TiN has high melting temperature (2950 °C), high microhardness (>20 GPa), good electric conductivity and high resistance to corrosion and oxidation.[1] These attractive physical and chemical properties suggest potentialities of TiN as a good reinforcement agent to the ceramic matrix. TiN-based ceramic is suitable for use as a coating for cutting and machining tools, a component for composites (TiN–SiC, TiN–W(Co), etc.) due to its high hardness, chemical stability and wear resistance.[2] The combination of high electrical resistance and high heat conductivity makes AlN powder the promising component for ceramic composites as well as for pure AlN dense ceramic.[3]

Combustion synthesis (CS) is the useful method for TiN and AlN production, because of non-expensive facility, high-rate exothermic synthesis reaction and wide range of synthesized products. A lot of studies concerning the efficiency of the CS method have been carried out and it was proved that the CS products cost much lower than that of the “furnace” technologies.[4] Usually, a higher nitrogen gas pressure during CS process leads to a higher conversion degree of metal (Ti or Al) to nitride (TiN and AlN). However, a complete conversion cannot be achieved by traditional CS at high pressure (10–500 atm) because of the metal melting before the combustion wave,[5] and the subsequent kinetic limitation of the nitrogen gas diffusion inside the melted metal. Diluents of different nature are generally used to enhance the Me → MeN conversion and the aim of diluents usage is reduction of the temperature of synthesis reaction.[2] The usage of a pure nitrogen as the nitridizing reagent assumes high pressure apparatuses and it strongly decreases the effectiveness of TiN and AlN synthesis by CS method. The possibility of air (instead of N_2) usage for nitrides obtaining was proved in our previous work.[6]

The dynamics of phase formation in the combustion wave of the “Ti–N_2” and “Ti–air” systems have been investigated in Ref. 7. It is shown in Ref. 7 that TiN synthesis during Ti combustion in air seems difficult, because an oxynitride phase appears on the sample surface almost immediately after TiN formation and TiN is further oxidized to TiO_2 due to high oxygen reactivity. The authors confirmed their results by time-resolved XRD,[7] but, contradictory result—the large amount of crystal nitride phases in the final combustion products was found in this work. The result was consistent with the previous our studies for powdery Al and Zr–Al combustion in air.[8,9]

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Table 1
The characteristics of initial powders

Powder	Particles size (mean surface)[a], a_s (μm)	Apparent density, ρ_{ap} (g/cm^3)	Specific surface area (BET), S_{sp} (m^2/g)	Particle shape
Ti	630	1.19	0.0023	Awkward shape, uneven surface
TiO_2	80	0.54	0.0240	Spheroidal
Al (ASD-4[b])	20	1.17	0.1300	Spherical
Al (PAP-2[c])	4	0.44	5.4000	Flaked

[a] Calculated from BET, assuming particle shape (for spherical particles $a_s \times S_{sp} \times \rho = 6$).

[b] Aluminum spherical dispersed.

[c] Pigment aluminum powder.

In the present work a large amount of TiN phase was obtained with combustion of "Ti–TiO_2" and TiN and AlN phases with combustion of "Ti–Al" mixtures in air under the atmospheric pressure. The "inert" (TiO_2) and "active" (Al) diluents were added to compare their effect on the nitrides formation by combustion. TiO_2 itself does not react with the Ti, but the mixtures "metal-oxide" were easily burnt in air by local ignition. The sample mass was chosen relatively high (10 g) to avoid the negative effect of the small sample mass on nitrides formation, which was not taken into account in Ref. 7. The formation mechanism of the non-equilibrium products—TiN and AlN appeared during combustion process was discussed in the work.

2. Experimental results and discussion

2.1. Powders characterization and mixtures preparation

The micron-sized Ti, TiO_2 and Al powders, purchased from "RUSAL" (Russia) were used in this work (Table 1). After the measurements of the powders (Fig. 1) characteristics, they were mixed in ethanol and dried with vacuum rotary evaporator. The samples on the basis of Ti powder were burnt in air (Table 2): I—"Ti–TiO_2" (inert diluent) mixtures; II—"Ti–Al" (active diluent) mixtures. All studied initial powders had large particles with the relatively low S_{sp}, instead of Al (PAP-2) powder, which, consequently, showed higher reactivity in combustion processes.

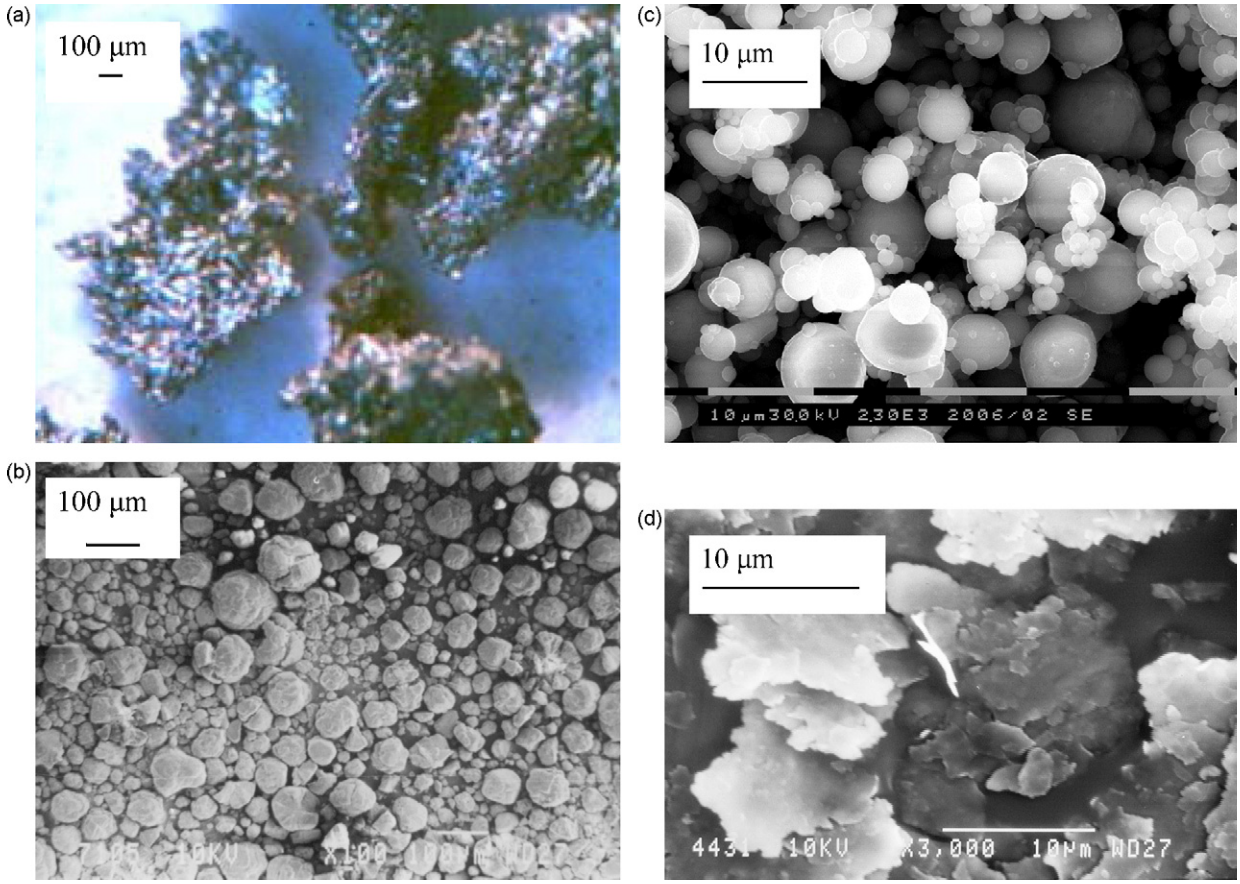

Fig. 1. SEM images of initial powders: a—Ti, b—TiO_2, c—Al (ASD-4), and d—Al (PAP-2).

Table 2
Initial powdery mixtures composition (“Ti–TiO_2” (I) and “Ti–Al” (II))

Mixture composition (wt.%)	
I	II
100 Ti–0 TiO_2	100 Ti–0Al
80 Ti–20 TiO_2	90 Ti–10 Al (ASD-4)
60 Ti–40 TiO_2	80 Ti–20 Al (ASD-4)
50 Ti–50 TiO_2 + 10 Al (PAP-2) (over 100)	70 Ti–30 Al (ASD-4)
40 Ti–60 TiO_2 + 10 Al (PAP-2) (over 100)	60 Ti–40 Al (ASD-4)
20 Ti–80 TiO_2 + 10 Al (PAP-2) (over 100)	50 Ti–50 Al (PAP-2)
10 Ti–90 TiO_2 + 10 Al (PAP-2) (over 100)	40 Ti–60 Al (PAP-2)
	30 Ti–70 Al (PAP-2)
	20 Ti–80 Al (PAP-2)
	10 Ti–90 Al (PAP-2)
	100 Al (PAP-2)

The particle size of diluent powders was selected of at least more than 5 times less than for the Ti powder (Table 1), because the Ti particles, being a burning initiator, should be covered by the diluent particles.

2.2. Powders burning

The all freely poured samples were burned in the shape of the cones. The combustion of “Ti–TiO_2” mixtures with the percentage of Ti $\leq$ 50 wt.% could not be initiated with the heated tungsten wire that is why a fine reactive aluminum powder (PAP-2) in quantity of 10 wt.% over 100 wt.% was added as an ignitor. The “Ti–Al” mixtures with the percentage of Al $\geq$ 50 wt.% were not initiated with the heated tungsten wire, that is why aluminum powder ASD-4 was replaced by aluminum powder PAP-2 completely (Table 2). The mass burning rate (Fig. 2) was calculated by Eq. (1):

$$v_b = \frac{m_s}{t_b} \qquad (1)$$

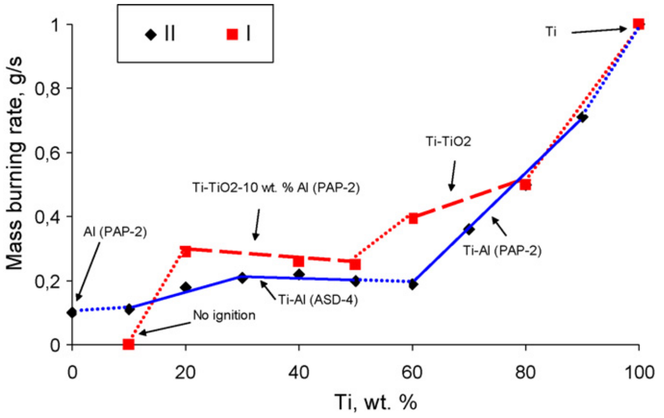

Fig. 2. Mass burning rate of the samples versus Ti content in initial powdery mixtures “Ti–TiO_2” (I); “Ti–Al” (II).

where m_s—sample weight expressed in grams; t_b—burning time expressed in seconds.

The data of the mass burning rate versus Ti content in initial mixture are presented in Fig. 2. The burning behaviour of the all samples corresponded to an one-stage heat explosion regime (Fig. 3), which is typical for “metal–gas” systems.[10] The mass burning rate for the compositions “Ti–TiO_2” (I, Table 2) was weakly dependent from the Ti metal content in the mixture in the range 0.2–0.5 g/s (Fig. 2), which could be caused by a high melting enthalpy for TiO_2 (67 kJ/mol for rutile). The addition of the Al (PAP-2) powder did not increase the burning rate significantly (Fig. 2). The curve of the mass burning rate (Fig. 2) for the mixtures of “Ti–Al” system (II, Table 2) could be divided into two parts because aluminum powders of different particles sizes were studied. The burning rate for “Ti–Al” system had weak dependence on the titanium content in the range up to 60 wt.% of Ti, but it appreciably increased at the changing of the coarsely dispersed aluminum powder (ASD-4) to finer one (PAP-2) (see Fig. 2).

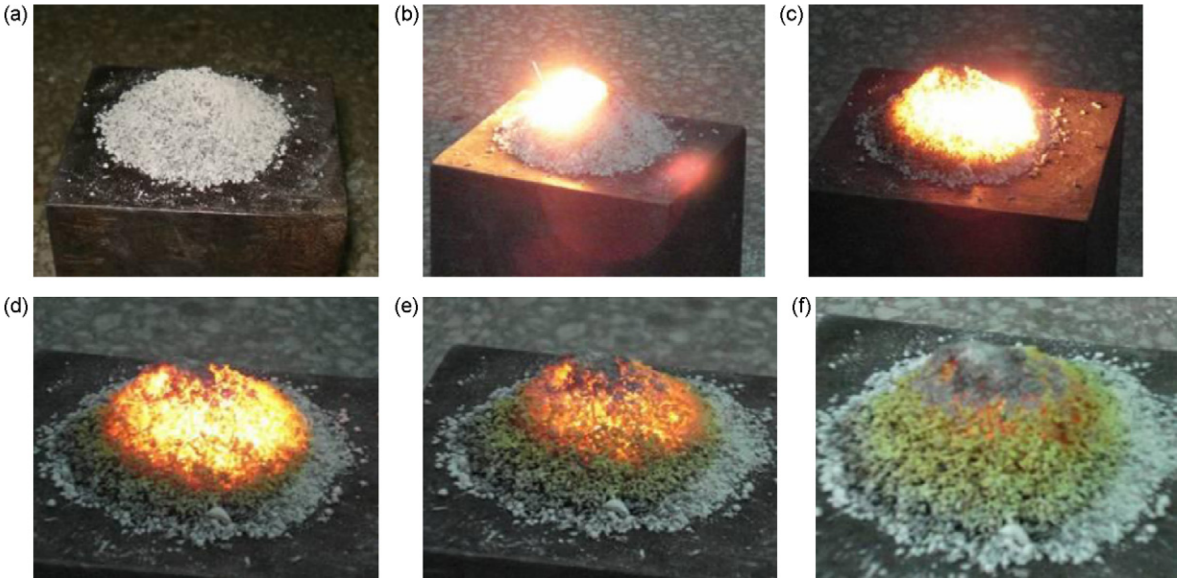

Fig. 3. Video images of burning process for the mixture (80 Ti–20 TiO_2), time from the ignition: a—initial sample; b—5 s; c—15 s; d—20 s; e—30 s; f—50 s.

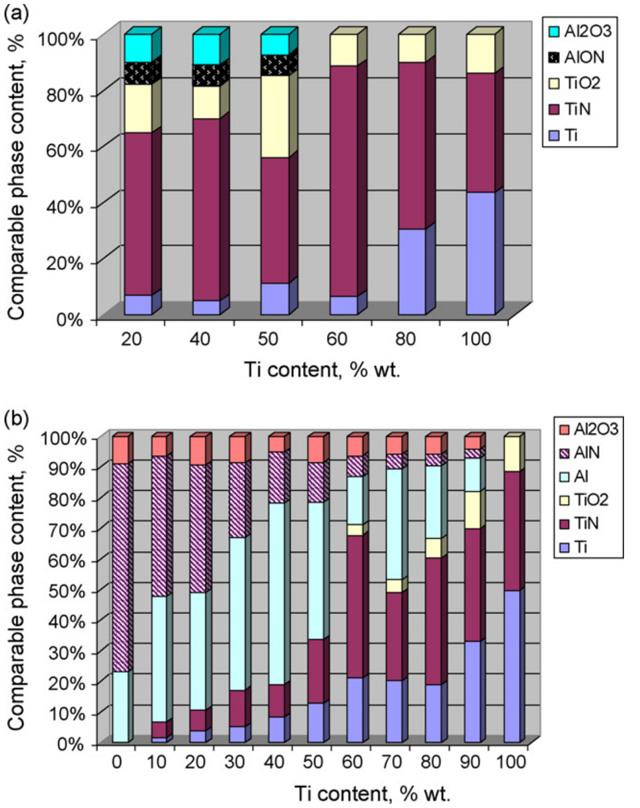

Fig. 4. Comparable phase composition (SIEMENS D 5005 diffractometer, Cu Kα) of the solid combustion products of mixtures "Ti–TiO_2" (a) and "Ti–Al" (b) versus percentage of the metal Ti in initial mixtures.

2.3. *Combustion mechanism for "Ti–TiO_2" mixtures (I, Table 2)*

The "cakes" of the solid combustion products were analysed by SEM and XRD (after disaggregation). The all "cakes" of the combustion products had the yellowish colour because of TiN presence as compared with the pure Al powder combustion. The results of XRD analysis (SIEMENS D 5005 diffractometer, Cu Kα monochromator, $\lambda = 1.54$ nm, $\upsilon = 4°$/min) for solid combustion products of powder mixtures "Ti–TiO_2" (I, Table 2) showed the presence of the predominant TiN phase in all composite mixtures (Fig. 4a). For the mixture "60 wt.% Ti–40 wt.% TiO_2" the XRD pattern corresponded to 98 wt.% of TiN, and unburnt Ti and TiO_2 were present in a trace quantity (Fig. 5). The TiN formation mechanisms were suggested from the analysis of phase content and SEM-images (JEOL 5600 F) of the burning products (Figs. 4a and Fig. 6).

If not to assume the unburnt metals, the process of nitrides formation determined the composition of the final combustion products. The TiN phase formation could be qualitatively described by the reactions (2)–(6) and similar to the previously reported process of the AlN formation with the Al–Al_2O_3 mixtures burning in air.[11] After ignition, the solid Ti starts reacting with the oxygen with the high heat release (2). The solid Ti melts (3) and reacts with nitrogen as the basic component of air (4). The other probable way for TiN formation is the reaction of the TiO, formed by the reaction (5), as an unstable compound and strong reducing agent, with air nitrogen (6).

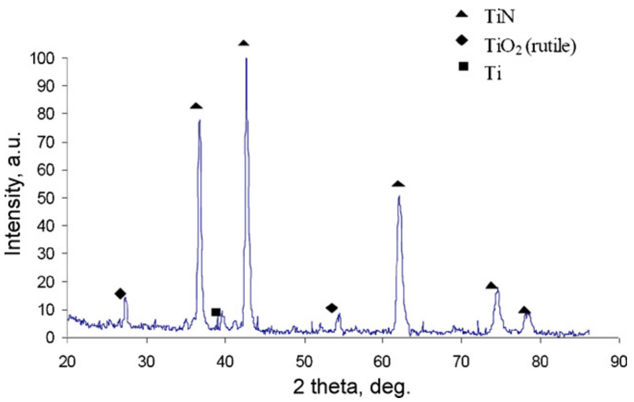

Fig. 5. Phase composition (SIEMENS D 5005 diffractometer, Cu Kα) of the solid combustion products of mixture "60 Ti–40 TiO_2": TiN (ICDD 06-0642), Ti (ICDD 05-0662), and TiO_2 (rutile ICDD 21-1276).

$$Ti_{(s)} + O_{2(g)} \rightarrow TiO_{2(s)} - 944\,kJ \qquad (2)$$

$$Ti_{(s)} \rightarrow Ti_{(l)} + 19\,kJ \qquad (3)$$

$$2Ti_{(l)} + N_{2(g)} \rightarrow 2TiN_{(s)} - 646\,kJ \qquad (4)$$

$$Ti_{(l)} + TiO_{2(l)} \rightarrow 2TiO_{(l)} - 108\,kJ \qquad (5)$$

$$2TiO_{(l)} + N_{2(g)} \rightarrow 2TiN_{(s)} + O_{2(g)} + 406\,kJ \qquad (6)$$

The combination of reactions (4) and (6) resulted in the high yield of TiN in the final combustion products, which was confirmed with SEM image of the Ti combustion products (Fig. 6): they formed through the liquid phase. Thus, the inert diluent TiO_2, could increase the yield of TiN in the final combustion products.

2.4. *Combustion mechanism for "Ti–Al" mixtures (II, Table 2)*

The phase composition of the combustion products (Fig. 4b) reflected the lower effect of the reaction (4) on the process of

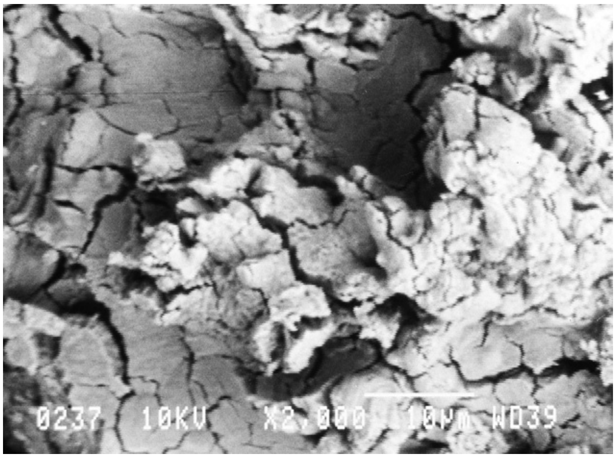

Fig. 6. SEM image of the porous "cake" of the solid combustion products of mixture "60 Ti–40 TiO_2".

TiN formation. Moreover, visually, Ti and Al burnt separately, because the burning rate of Ti (Eqs. (2) and (4)) in air was much higher than for Al (Fig. 2). In fact, already burning Ti particles ignited the Al particles, the total heat release in the burning system became lower, because the heat was consumed to Al melting (7) that is why it resulted in a worth interaction with nitrogen for the both metals.

$$Al_{(s)} \rightarrow Al_{(l)} + 10\,kJ \qquad (7)$$

The role of the active diluent (Al) in the TiN formation by Ti combustion in air was negative on the yield of both TiN and AlN. The mechanism of AlN formation in air by Al burning has been described[9] and it also assumes to liquid-phase reactions, which are also typical for LaN,[12] GaN[13] and BN[14] formation by corresponding metals combustion in air. Hence, the new class of chemical reactions of non-equilibrium products (nitrides) formation for high exothermic III–IV metals combustion in air should be established.

3. Conclusion

The possibility of TiN powder obtaining with the coarsely dispersed Ti powder combustion in air was shown in this study. The yield of TiN produced by CS in air was higher than those reached by the Ti powders burning in pure nitrogen.[15] The experimental approach used in this work is much simplified—freely poured powders used and air applied as the source of nitrogen. Hence, the CS of TiN in air is more attractive than in nitrogen. However, the problem of large amount of residual Ti in the burning products still exists. The mechanism of TiN formation, the most probably assumes participation of the intermediate product TiO with the high reducing ability.

Acknowledgements

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