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Influence of humidity on the combustion of powdered and granulated Ti + 0.5 C mixtures

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The combustion of both powdered and granulated Ti + 0.5 C mixtures at various moisture contents in an initial mix as in argon flow (coflow filtration) and without gas flow has been ascertained. The combustion velocity of 'wet' Ti + 0.5 C powder in an argon flow under 1 atm pressure difference decreases almost by one half in comparison to 'dry' mixture, while for granulated mixtures the moisture influence on combustion velocity and phase structure of the final products is insignificant.

The convective-conductive mechanism of combustion[1–3] was earlier established for fast-burning powder systems (Ti + C, Ti + 0.5 C, Ni + Al, *etc*.), according to which the speed of penetration of a melted reagent into initial powder is the velocity of combustion wave propagation. Thus, convective heat transfer is caused by a current of a melted layer of fusible reagent under both capillary forces and pressure difference of impurity gases before and behind the melted layer.[4] In terms of the convective-conductive mechanism, the presence of moisture in the initial powder sample can be considered as a source of impurity gases affecting the combustion velocity.[4] The role of small additives in solid-phase combustion is much more complicated than in combustion of coal powders in a gas phase.[5,6]

To exclude the formation of a low permeable melted layer providing convective heat transfer and strong influence of gas impurities emission on burning velocity in the course of combustion, the granulation of an initial powder mixture was used.[7,8] In this case, the movement of the melted reagent under capillary forces is limited within a granule; *i.e.*, the continuity of the porous environment is completely missing. It provides a high permeability of the sample both in the course of combustion and after its cooling.[7,8] Therefore, a decrease in the influence of gas impurities (*e.g.*, water vapour) on combustion velocity can be observed. Even if difference in combustion velocities with the use of various soot brands centres around various content of gas impurities in soot, then granulation can also lead to reduction in the influence of the soot brand on combustion velocity.

For experiments, we selected a fraction with particle sizes between 0.63 and 2 mm.[†] The combustion of samples was performed in the experimental installation (see Figure S1, Online Supplementary Materials), which allowed burning samples in gas flow, controlling gas flow and gas pressure in the course of combustion, and also obtaining videos of combustion process.[‡] Combustion velocity was determined on the basis of time-lapse processing of the videos.

In the experiments, a bright front of combustion extending over a sample of 'dry' Ti + 0.5C (soot) powder without gas flow was observed. It was established that the dependence of position of the combustion front on time is linear; combustion velocity was 4.1±0.4 mm s^{-1}. The combustion of the sample was accompanied by noticeable gas emission which was completed simultaneously with achievement of the bottom end face of a sample by the combustion front. The X-ray phase analysis of combustion products of a dry Ti + 0.5C sample showed that the product consists of two phases: nonstoichiometric titanium carbide and Ti.

A 2 wt% water additive to the initial Ti + 0.5C powder leads to insignificant reduction of combustion velocity (Figure 1). Since water additive provides non-stationary combustion, then average combustion velocity (length of a sample was divided to combus-

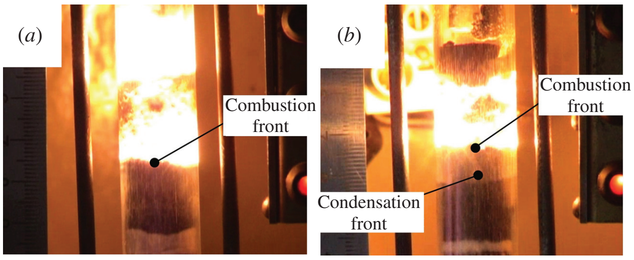

Figure 1 Combustion of Ti + 0.5C powder under gas flow conditions with different moisture contents of the sample: (*a*) 'dry' and (*b*) 'wet' (2% moisture) samples.

[†] Commercial Ti powders (PTS brand), carbon black (P803-T brand) and synthesized titanium carbide were used. Fractional powder composition and particle size distribution in powder were determined by a standard technique with MicroSizer 201. The Ti + 0.5C powder mix was dried up (humidity was supervised with Elviz-2C); then, it was humidified up to 2 wt% water by means of a KROMAX Q-403 steam generator. The water content of a sample was supervised by a weight method using an Acom Jw-1 balance.

The granulation of powders was performed as described below. First, Ti + 0.5C powder blends were processed in a drunk barrel mixer for 30 min. Then, a solution of 4 wt% polyvinyl butyral in ethanol was added to the processed blend. The thus prepared paste-like mass was rubbed through a sieve (1 mm mesh) and then rolled on a horizontal surface to provide spherical granules. After drying, the granules were separated with a vibrosieve.

[‡] To create pressure difference at sample end faces, a gas flow was supplied from the top end face at 2 atm *via* a three-position switch, at the bottom end face pressure made up 1 atm. A sample was placed in a vertical quartz tube 19 mm in diameter and 90 mm in length on a two-layer substrate of quartz sand and mineral Al_2O_3 wool. Signals from sensors and a thermocouple were recorded along with filming. The combustion was initiated from the top end face of the sample by means of a quickly heated spiral. Filming was performed with a Sony DCR-HC96E digital video camera and saved in computer memory. To exclude sample shrinkage in the course of combustion and for better reproducibility, porous samples before ignition were flushed with an Ar flow with a 1 atm pressure difference. X-ray analysis was performed with the use of a DRON 3M diffractometer.

tion time) was determined. The product also consists of the two phases of nonstoichiometric titanium carbide and Ti. X-ray phase analysis testifies that, in comparison with dry mixture, the presence of moisture leads to a twofold increase in both the relative intensity of Ti peaks in reaction product and small angle shifts.

Thus, both the experimentally observed reduction of combustion velocity and deterioration of possibility for melted Ti to spread in the sample, caused by the presence of moisture, are first associated with an increase in gas impurities emission rather than with reduction of thermal effect of reaction. To check this assumption, an inert diluent (4 wt% titanium carbide) was added to Ti + 0.5C powder instead of 2 wt% moisture. The amount of titanium carbide was chosen to provide the equality of heat quantity necessary for evaporation of 2 wt% moisture to heat quantity necessary for heating the inert additive up to the combustion temperature. Combustion velocity in the sample containing 4 wt% TiC was 4.0 mm s^{-1}.

Therefore, the main difference of combustion of the sample diluted with titanium carbide from the sample containing moisture implies that in the first case layer-by-layer stationary combustion takes place, as well as in the combustion of the 'dry' sample. This difference indicates different mechanisms of the influence of gas emitting and completely inert diluents on combustion.

X-ray phase analysis testifies that, in comparison with the powder sample without a diluent, the presence of 4 wt% TiC leads to an increase in the relative intensity of Ti peaks in the reaction product, similarly to the sample containing 2 wt% moisture. Thus, the close values of combustion velocity for the samples containing 4 wt% TiC and Ti + 0.5C without a diluent point to reduction of thermal effect of the reaction.

Further experiments were performed under conditions of an argon gas flow. We have shown earlier for Ti + 0.5C powder samples[1] that a pressure difference at the sample top and its bottom causes a marked increase in combustion velocity and, correspondingly, growth of the warming up zone. In addition, an inert gas flow removes gas impurities emitted from the reaction zone in the course of combustion.

It was found that the Ti + 0.5C powder sample after combustion in an argon flow showed shrinkage[1] and that a change of the sample longitude (shrinkage) occurred behind the combustion front; the combustion velocity was 10 mm s^{-1}. The analysis of gas samples taken below flow and pressure sensors showed that argon was present in gas phase at combustion stage. It testifies to the permeability of combustion front for Ar stream. The X-ray phase analysis revealed that the condensed combustion product (under flow conditions) consists of nonstoichiometric titanium carbide and Ti phases as in the previous case.

A 2 wt% moisture additive to Ti + 0.5C powder led to a decrease in combustion velocity [Figure 2(*a*)]. According to X-ray phase analysis, the product consists of the nonstoichiometric titanium carbide and Ti phases. However, unlike the samples burned down without a gas flow, no changes were observed in the relative intensity of peaks or angle shifts of titanium in the reaction product under argon flow conditions despite of the presence or lack of moisture in an initial sample.

The video filming of the combustion of 'wet' samples clearly demonstrated the occurrence of a condensation front ahead of the combustion front [Figure 1(*a*)]. This front is missing in the filming of 'dry' samples [Figure 1(*b*)]. The combustion velocity for Ti + 0.5C samples containing 4 wt% titanium carbide in argon was 8 mm s^{-1}. Such a value close to that of the sample without diluent (10 mm s^{-1}) is additional evidence of an insignificant reduction of reaction thermal effect related to the presence of diluent [Figure 2(*b*)].

The combustion velocity of the 'dry' granulated Ti + 0.5C sample without a gas flow was 8 mm s^{-1}, and that under gas flow conditions was 9 mm s^{-1}. The velocities of combustion of 'wet' granulated Ti + 0.5C samples also weakly depend on pressure difference (7–9 mm s^{-1}) [Figure 2(*b*)].

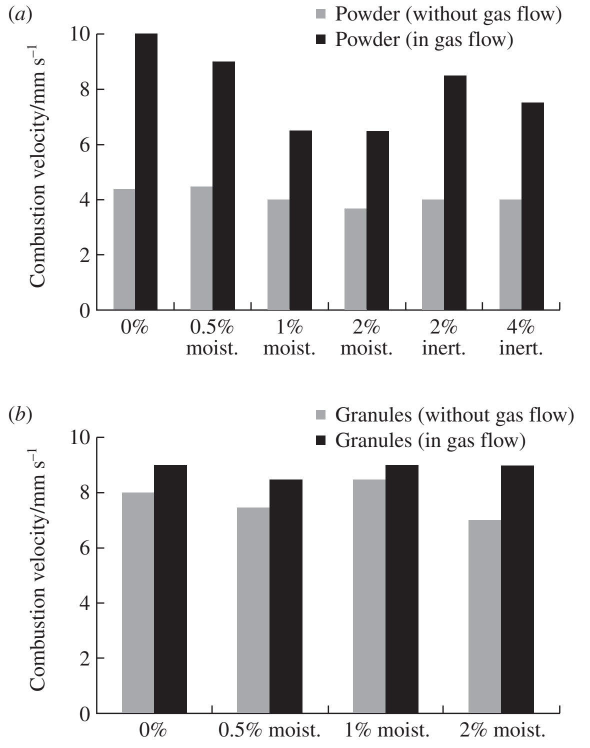

Figure 2 Combustion velocities over Ti + 0.5C (*a*) powder and (*b*) granulated samples *vs*. synthesis conditions and amount of moisture.

Close burning velocities of the granulated structures evidence a slight influence of gas impurities on flame propagation velocity. The analysis showed that irrespective of presence or lack of moisture in the sample reaction products (nonstoichiometric titanium carbide and Ti) are almost identical under gas flow conditions. The loss of moisture from granules in the course of drying is not probable since the granules become almost impenetrable for water.[8]

For evident demonstration of slight influence of gas impurities on burning velocity of granulated structures, two different brands of soot (P803-T and P804-T) were used to prepare Ti + 0.5C samples. The burning velocities of powder samples (without additives) for P804-T and P803-T without Ar flow differed several times (1.5 and 4.4 mm s^{-1}, respectively), however the burning velocities of the granulated mixes differed slightly (7–9 mm s^{-1}) (Figure 3). Therefore, the use of granulated samples reduces effect of gas impurities emission including humidity both on the combustion velocity over the sample and on phase structure of the final products.

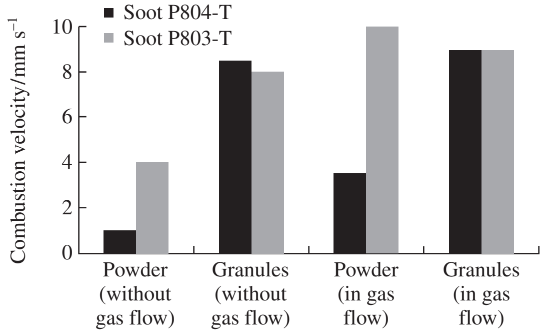

Figure 3 Combustion velocities in Ti + 0.5C 'dry' powder and granulated samples for different synthesis conditions and soot brands.

Thus, the presence of moisture does almost not affect the phase structure of the combustion products of granulated Ti + 0.5C samples. Under the conditions of an Ar coflow, the influence of humidity on the phase structure of reaction products decreases and the combustion velocity of the powder sample increases. The presence of moisture in the Ti + 0.5C powder sample affects the phase structure of combustion products and has almost no influence on the combustion velocity of the sample without a gas flow. The experimental data can be explained in terms of a convective-conductive combustion mechanism, which accounts for an essential role of both a melted reagent and impurity gas emission in the combustion wave propagation mode.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.019.

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