PROPAGATION OF A COMBUSTION FRONT OVER THE SURFACE OF METAL POWDERS WITH DILUENTS

E. V. Chernenko and L. F. Afanas'eva

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An experimental study of the effect of foreign inclusions of both chemically active materials, capable of burning in an air atmosphere and inert oxide materials on the propagation of a combustion front over the surface of titanium powders was carried out. It has been established how the character and the rate of surface combustion V_c of titanium powders change upon their dilution, depending on diluent concentration, melting temperature, disperse composition, and chemical activity.

The objective of the current study was to reveal the regularities of the change in V_c of metal powders with change in the content of foreign additives in them. Furthermore, it was of interest to detect various modes of surface propagation of the combustion front and to ascertain whether there is a linkage between the character of the change in V_c and the change in the critical ignition temperature T_{cr} for the same powder materials. This study also pursued a practical goal, namely, providing fire-explosion safety of industrial production. Since powder metallurgy employs metal powders with additives of various kinds, one should know how the additives will affect the rate of combustion propagation over a powder located in an apparatus or production area in an emergency.

Experimental Procedure. Investigations were carried out on a setup described in [1]. A powder of the material considered was poured on a metal substrate. The charge was 40 mm wide, 6 mm thick, and 300 mm long. The passage of the combustion front over the powder was recorded with the help of eight FD-8G photodiodes, and the temperature in the combustion front was determined using a tungsten-rhenium thermocouple. Combustion of the powder was initiated by a nichrome spiral to which electric current was applied. The investigations were conducted in an air atmosphere, with the substrate positioned horizontally. PTS-1-93 and PTM pr. 6 titanium powders were employed in the work. As a diluent, we chose the following powders: Ni of the type PNE-1 < 5 μ m; Cu of the type PMS-1 < 50 μ m; Mg of the type MPF-1; Al of the type ASD-1; W of the type PVN; Ta of the type TU 95-318-75; B_2O_3 of the state standard 10068-25; TiO₂ of the type TU 95-318-75; and Li_2O_2 of the type TU 6-02-770-79. For studying the effect of inert additives to the titanium powder we selected SiO₂ powders of various fractions < 400 μ m. Thermodynamically, oxidation-reduction reactions can proceed in the Ti+SiO₂ system [2]. However, as investigations have demonstrated, the structure of the front of surface combustion of titanium powders is three-stage [1], and the maximum temperature of the first stage does not exceed 1600°C, i.e., is lower than the melting temperature of Ti, TiO₂, and SiO₂. Therefore, it may be assumed that, with titanium diluted with silica, even if an oxidation-reduction reaction does proceed, it cannot contribute markedly to the propagation of surface combustion of titanium powder.

Experiments on the ignition of powder materials were performed on a setup described in [3]. A powder sample of bulk density was placed in a capsule made of a brass gauze (with a mesh size of 71 μ m) and was introduced into a metal unit heated in a muffle furnace. The capsule inner diameter and length were 6 and 20 mm. A gas (air), heated to the furnace temperature, was blown through the unit at a speed of 8.7 m/sec. The temperatures of the sample and the unit were measured by Chromel-Alumel thermocouples. T_{cr} (the temperature within the unit at the sample site below which no ignition occurred) was determined to an accuracy of $\pm 5^{\circ}$ C, with a confidence level of deviation of the results from the arithmetic mean of 95%.

Results and Discussion. Figure 1 shows V_c of titanium (PTM pr. 6) vs the content of the inert additive SiO₂ in it. Clearly, with an insignificant dilution of the titanium powders, the rate of their surface combustion rises.

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Fig. 1. Rate of surface combustion propagation vs diluent percentage C (wt. %) in a mixture with a titanium powder: a: 1) Ti (125-160 μ m) + SiO₂ (> 315 μ m); 2) Ti (125-160 μ m) + SiO₂ (160-315 μ m); 3) Ti (125-160 μ m) + Ni (< 5 μ m); 4) Ti (125-160 μ m) + SiO₂ (125-160 μ m); 5) Ti (125-160 μ m) + SiO₂ (80-125 μ m); 6) Ti (> 315 μ m) + SiO₂ (160-315 μ m). a) V_c, cm/sec; b) V_c, mm/sec.

Here, as the particle size of the diluent increases at the same concentrations of it in the mixture, V_c increases. Experimental data may be accounted for as follows. It was discovered that, after passage of the combustion wave over the titanium powder, on the surface a loose layer of burnt titanium forms, under which a continuous layer of metal sintered during passage of the combustion front lies. Upon dilution with an inert material, the loose layer becomes thicker, whereas with a ~20% dilution after the combustion wave has passed, there is no continuous metal layer. Therefore, only the top layer of the titanium powder participates actively in combustion propagation over the powder surface. When an inert diluent with a high melting temperature is added to titanium, the particles of the inert material hinder sintering of the metal particles, thereby extending the active layer of the powder. As a result of an increase in the mass of the powder participating in combustion, under the same conditions of heat removal the temperature of the combustion front rises, which also causes V_c to increase. With large additives of the inert material, an ever more significant part of the heat from titanium combustion goes into heating the inert particles, which leads to a decrease in V_c , and with very large dilutions with the inert material the titanium combustion becomes impossible.

It is seen from Fig. 1a that instances where there is a noticeable rise in the surface combustion rate even with appreciable titanium dilution (> 5% diluent) can occur. This is connected with stratification of the mixture prepared for the tests. During the preparation of the mixture layer for the tests, smaller diluent particles collapse between large particles of the titanium powder. Because the surface layer of the mixture is composed solely of titanium particles at small diluent concentrations, the diluent does not exert a significant effect on V_c . With increasing diluent concentration, a constantly rising number of particles of the added material find their way into the upper region of the tested layer, which also causes V_c to change.



Fig. 2. Critical ignition temperature, $^{\circ}C$, vs diluent percentage (wt. %) in a mixture with a titanium powder.

It is noteworthy that the effect obtained in the experiment, manifests itself only when diluents with a high melting temperature are employed. When diluents with a low melting temperature are used, e.g., B₂O₃ (Fig. 1b), V_c does not increase. It is evident from Fig. 1 that, with increasing diluent concentration in the mixtures, the curve of change in V_c passes through an inflection point at diluent concentrations of $\sim 10-35\%$. Such a form of experimental curves indicates a change in the mechanism of combustion propagation. Numerical evaluations show that, at high propagation rates of the combustion front, the width of the Michelson zone is comparable with, and even smaller than, the size of the grains making up the powder, if, of course, the evaluations use the thermal conductivity characteristic of the powder material rather than of an individual grain, i.e., by virtue of the high thermal conductivity of the metal, the width of the Michelson zone is equal to the size of the particles composing the titanium powder. In this case, a combustion mode that can be conventionally called a mode of sequential firing is realized. When the combustion rate changes due to thermal dilution, the width of the Michelson zone increases and, as a result, ahead of the combustion front a wide layer particles that undergo a stage of "slow" heating prior to ignition forms. Drawing a further analogy with ignition theory, this combustion mode may be referred to as a mode of sequential ignition. In the second case, at a relatively long heating stage, on a titanium particle a protective oxide layer that slows down its oxidation and, hence, ignition manages to build up. The lower is V_c , the more significant is the effect of a preignition low-temperature oxidation. This effect is indicated by the inflection of the curves (Fig. 1).

Near the limit of combustion front propagation, the third, spin combustion mode was detected. Unlike classical spin combustion, this combustion mode is realized not on a cylindrical sample but, instead, on a plane. As the combustion limit is approached by the dilution method, the combustion front undergoes a modification. Incandescent areas appear in it, whose size is comparable with the sizes of the particles making up the powder. These areas move across the powder layer, i.e., along the combustion front. With increasing dilution, the number of incandescent points gradually diminishes. Here, on the sinter that remained after passage of the combustion wave, uniformly alternating bands with different degrees of material burnup are exhibited ever more clearly, which is also observed visually.

When studying mixtures of titanium powders with other metal powders it was found that often, as in the case with inert diluents, an increase in V_c occurs when small additions of other powders are made to titanium. With increasing diluent concentration, a wide concentration region, in which the rate of surface combustion varies slightly may exist (for example, Ti + Ni and Ti + W (Fig. 1)). These results are explained by the fact that three reactions proceed in the mixtures concurrently: titanium oxidation, oxidation of the added metal, and an intermetallic reaction [4], and weakening of the role of one reaction may be compensated for by the presence of the other two to some extent.

A titanium-magnesium mixture proved interesting. V_c of this mixture is smaller than V_c of its individual components over a wide range of concentrations of the components (Fig. 1b), since the leading reaction in this concentration range is a reaction of vapor-phase oxidation of magnesium. Burning magnesium vapor cuts off the air oxygen from titanium, i.e., titanium fulfills the role of an inert diluent of magnesium here. Such an explanation is also supported by the fact that a continuous loose layer of magnesium oxide was detected on the surface of burnt samples.

Figure 2 gives T_{cr} of the mixtures considered. The main conclusion that might be drawn from comparing Fig. 2 and Fig. 1b is that no direct relation of T_{cr} to V_c , common to all mixtures, was found. The rate of surface combustion can decrease both with decrease and increase in T_{cr} , although, purely qualitatively, this relation can be traced for individual mixture compositions. For example, the presence of a plateau on the curve corresponding to a Ti + Al mixture (Fig. 2) corresponds to the presence of a plateau on the V_c curve (Fig. 1b), although the concentration ranges are also different here. It is noteworthy that, proceeding from the a knowledge of T_{cr} , nothing can be said about the change in V_c without experimental investigations. We give the following example. When titanium is diluted with a lithium peroxide powder, T_{cr} gradually decreases to 35° C in the region with up to 5%peroxide and further, it increases only by 10° C in the region with a perioxide content of up to 50%, i.e., it virtually does not change. In studying the same mixtures to determine of V_c , it was found that there are no changes in V_c with a peroxide content in the mixture of up to 5%, whereas with a further increase in the lithium peroxide concentration in the mixture V_c starts increasing dramatically, and at 20% peroxide it is already two orders of magnitude larger than V_c of a pure titanium powder.

CONCLUSIONS

1. Foreign high-melting additives to titanium powder accelerate its surface combustion at small concentrations ($\sim 5\%$).

2. With increasing particle size of a high-melting additive the rate of surface combustion rises at the same concentrations.

3. As titanium powder is diluted with other powder materials, there can be sequential replacement of three combustion modes: sequential firing, sequential ignition, and the spin mode.

4. There are material mixtures whose surface combustion rate is lower than that for each individual component.

5. There is no general relationship between the rate of surface propagation of a combustion front over a powder and the critical ignition temperature.

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