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LAWS AND MECHANISM OF DIFFUSIONAL SURFACE BURNING OF METALS

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As shown in [1], burning metal powders in a nitrogen medium is an effective means of obtaining the high-melting nitrides widely used in modern technology. Accordingly, the study of the combustion mechanism of metal-gas systems is of considerable interest. The laws of diffusional metal combustion were first studied in [2, 3]. On the basis of the experimental data obtained certain ideas about the combustion mechanism were formulated. The limit regime of diffusional surface burning, in which gas is supplied to the combustion front solely through the ends of the specimen, and the lateral surface is impermeable, was subjected to a detailed theoretical study in [4-6].

In the present research diffusional surface burning regimes were studied experimentally. This not only made possible a comparison with the theoretical results but also provided more detailed information about the combustion mechanism.

From the methodological standpoint, the system tantalum–nitrogen proved the most convenient to investigate. Tantalum is easily pressed, the specimens remain permeable after passage of the combustion wave, etc. Moreover, it is a multiphase system and, as shown in [7], the combustion products may be γ-Ta_2N, hexagonal ε-TaN, or cubic δ-TaN. This gives it additional scientific and practical interest.

Experimental Method

In the experiments we used >99% pure tantalum powder with a particle size < 10 μm, and high-purity nitrogen containing $< 0.001\%$ oxygen. The tantalum powder was pressed into quartz tubes or cylinders 4-20 cm long, about 1 cm in diameter, and with a wall thickness ≤ 0.05 cm. The relative density of the pressings (Δ) was kept constant and equal to 0.2. The nitrogen was supplied either only through the starting tantalum powder toward the combustion front or only through the combustion products. A series of experiments was performed on specimens open at both ends. In the first case, to eliminate the supply of nitrogen through the combustion products, we used tubes with a flange at the top, to which an ebonite cap with electrodes for initiating combustion was tightly fitted. In the second case we used quartz cylinders.

The nitrogen pressure was varied from 20 to 3000 atm. At low pressures (up to 100 atm) the experiments were carried out in a constant-pressure bomb [8], at high pressures in a high-pressure apparatus designed at the Institute of Chemical Physics of the Academy of Sciences of the USSR. The specimens were mounted vertically in the bomb; combustion was initiated at the top of the specimen.

The combustion temperature was varied by introducing a certain amount of end product into the starting tantalum powder. The burning rate was recorded with an FR-11 photorecorder and by the burning wire method [9]. The nitrogen content of the combustion products was determined by the Kjeldahl method, and for the x-ray phase analysis we used a DRON-2.0 apparatus.

Experimental Results

Nitrogen Flow Counter to Combustion Front. In this case propagation of the combustion wave through specimens 4 cm long was observed only at $p_{N_2} \geq 20$ atm, and through specimens 20 cm long only at $p_{N_2} \geq 60$ atm. At nitrogen pressures up to 100 atm the combustion process could be observed through the bomb glasses and the burning pattern was as follows: Initiation of the reaction was followed by the appearance of a faintly luminescent combustion front whose velocity and brightness increased as the open end of the specimen was

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Chernogolovka. Translated from Fizika Goreniya i Vzryva, Vol. 15, No. 4, pp. 9-17, July-August, 1979. Original article submitted September 25, 1978.

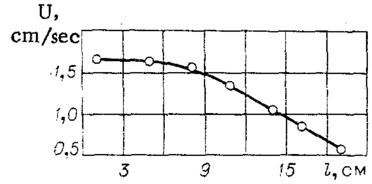

Fig. 1

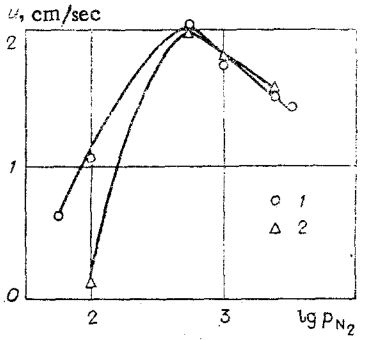

Fig. 2

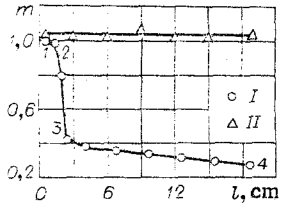

Fig. 3

Fig. 1. Burning rate vs distance to open end of specimen (l_{sp} = 20 cm, p_{N_2} = 60 atm).

Fig. 2. Average burning rate vs nitrogen pressure. 1) Counterflow of gas; 2) gas supplied through combustion products.

Fig. 3. Extent of reaction vs distance to open end of specimen (l_{sp} = 20 cm). I) p_{N_2} = 60 atm; II) p_{N_2} = 500 atm. Phase composition of products: 1-2) δ-TaN_{cub}; 2-3) ε-TaN_{hex}, γ-Ta_2N_{hex}, solid solution of N_2 in Ta; 3-4) γ-Ta_2N_{hex}, solid solution of N_2 in Ta.

approached. When the front reached the bottom of the specimen there was a flash, then a second brighter combustion front appeared, traveling more slowly in the opposite direction. After traveling 0.5-1 cm it disappeared.

A typical graph of burning rate vs the distance to the open end is reproduced in Fig. 1. This curve was obtained for specimens 20 cm long; for shorter specimens, as follows from the figure, the unsteadiness of the propagation velocity was less sharply expressed.

As the pressure increases, combustion becomes more intense. The average burning rate* increases, reaching a maximum (about 2 cm/sec) at 500 atm, then begins to decrease. The pressure dependence of the average burning rate is shown in Fig. 2. At $p_{N_2} \geq 500$ atm the burning rate may be assumed to be steady, although in certain parts of the specimens it varied somewhat.

We carried out chemical and x-ray phase analyses of samples taken at various distances from the open end of the burnt specimens. A typical plot of nitrogen content vs distance to the open end is reproduced in Fig. 3. Clearly, as this distance decreases, the nitrogen content, like the burning rate, increases. In the layer where the reverse front stopped, the extent of reaction increases sharply to complete.†

The x-ray phase analysis showed that in the first combustion front γ-Ta_2N_{hex} and a solid solution of nitrogen in tantalum are formed. As the distance between the front and the open end decreases, the amount of γ-Ta_2N_{hex} increases, and the amount of solid solution of nitrogen in tantalum decreases. In the layer where the reverse front stopped, the combustion product is three-phase; ε-TaN_{hex} was also detected. The next layer is actually single-phase, containing only δ-TaN_{cub}.

As the pressure increases, the form of the relation between nitrogen content and the distance to the open end remains qualitatively the same, although the average amount of nitrogen in the combustion products formed in the first and second fronts increases. Only at $p_{N_2} \geq 500$ atm does the extent of reaction (complete) remain constant along the length of the specimen, and the combustion product is single-phase, only δ-TaN_{cub} being detected (Fig. 3).

Nitrogen Supplied through Combustion Products. The combustion behavior of tantalum pressed into cylinders differs essentially from that observed when the nitrogen flows counter to the combustion front. In this case we observed only one bright combustion front, which traveled increasingly slowly through the specimen. At a specimen length of 4 cm the front did not reach the bottom of the specimen even at p_{N_2} = 100 atm. In this case the average burning rate on an initial section of about 0.5 cm did not exceed 1-2 mm/sec, but as the pressure rose it increased substantially. At $p_{N_2} \geq 500$ atm specimens 20 cm long burned to the end, the burning rate being steady and coinciding with the burning rate of specimens open at the "cold" end (Fig. 2).

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* $u_{av} = l/t$, where l is the specimen length, t is the time taken by the combustion front to travel through the specimen.

† To be specific, we shall assume that the reaction is complete when the combustion products are ε-TaN_{hex} and δ-TaN_{cub}.

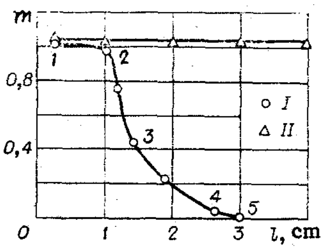

Fig. 4

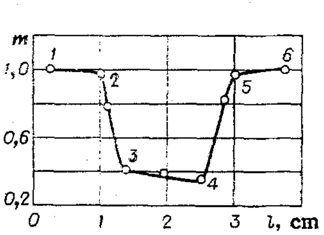

Fig. 5

Fig. 4. Extent of reaction vs distance to open end of specimen. I) l_{sp} = 4 cm, p_{N_2} + 100 atm; II) l_{sp} = 20 cm, p_{N_2} = 500 atm. Phase composition of products: 1-2) δ-TaN_{cub}; 2-3) ε-TaN_{hex}, γ-Ta_2N_{hex}, solid solution of N_2 in Ta; 3-4) γ-Ta_2N_{hex}, solid solution of N_2 in Ta; 4-5) solid solution of N_2 in Ta.

Fig. 5. Extent of reaction vs distance to bottom of specimen (l_{sp} = 4 cm, p_{N_2} = 60 atm). Phase composition of products: 1-2, 5-6) δ-TaN_{cub}; 2-3, 5-4) ε-TaN_{hex}, γ-Ta_2N_{hex}, solid solution of N_2 in Ta; 3-4) γ-Ta_2H_{hex}, solid solution of N_2 in Ta.

The profile of nitrogen concentration in the end products is shown in Fig. 4. It is noteworthy that, although the visible combustion front stopped after about 1 cm, the tantalum-nitrogen reaction continued over a much greater distance (about 3 cm). Complete reaction was achieved only up to the point at which the visible front stopped, beyond this as the distance to the open end increased the nitrogen content fell smoothly to zero.

The phase composition of samples taken at different distances from the open end was also different. Up to the point at which the visible front disappeared the structure of the samples was single-phase (δ-TaN_{cub}); this was followed by a three-phase region (γ-Ta_2N_{hex}, ε-TaN and solid solution of nitrogen in tantalum) and then by a fairly extensive region containing γ-Ta_2N and solid solution of nitrogen in tantalum. Next came a region with nitrogen–tantalum solid solution of variable composition and pure unburnt tantalum.

At $p_{N_2} \geq 500$ atm the extent of reaction does not depend on the distance to the open end, and the product is single-phase (δ-TaN_{cub} only).

Nitrogen Supplied through Starting Material and through End Product. The experiments were performed on short (4 cm) and long (20 cm) specimens. In the short specimens, after initiation of the reaction, a combustion front appeared and began to travel downwards with acceleration. However, this was immediately followed by the appearance of a second front which also traveled downwards, but with deceleration. When the first front reached the bottom of the specimen, a reverse front appeared. The second front and the reverse front, after traveling about 1 cm, died out. The nitrogen concentration profile of the burnt specimens is reproduced in Fig. 5. Clearly, at the ends of the specimen the reaction is complete; in the middle the nitrogen concentration is low, only γ-Ta_2N_{hex} and a solid solution of N_2 in Ta being present.

A comparison of Figs. 3 and 5 reveals that in principle the combustion of specimens open at both ends is the same as that of specimens open at the "cold" end, since the second front that develops at the top acts as a "plug" preventing nitrogen from reaching the layers where the reaction is incomplete until the end product δ-TaN_{cub} is formed there.

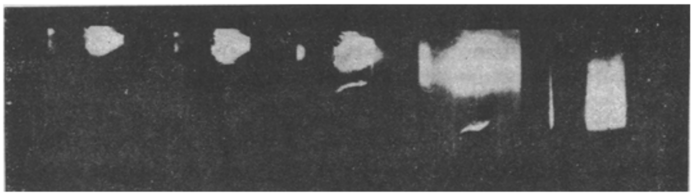

Fig. 6. Motion picture record of the front splitting effect (l_{sp} = 20 cm, p_{N_2} = 60 atm).

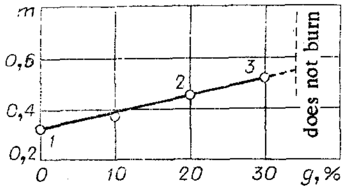

Fig. 7

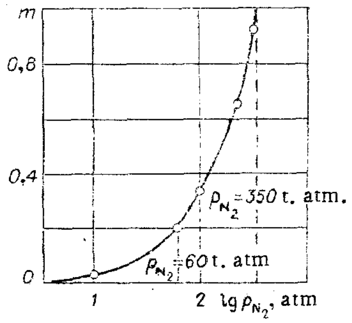

Fig. 8

Fig. 7. Extent of reaction vs dilution with a mixture of γ-Ta_2N_{hex} and a solid solution of N_2 in Ta (l_{sp} = 4 cm, p_{N_2} = 60 atm). Phase composition of products: 1-2) γ-Ta_2N_{hex}, solid solution of N_2 in Ta; 2-3) ε-TaN_{hex}, γ-Ta_2N_{hex}, solid solution of N_2 in Ta.

Fig. 8. Calculated pressure dependence of the possible extent of reaction due to pore nitrogen alone.

By increasing the length of the tube to 20 cm, it is possible to observe a combustion process similar to that when the nitrogen is supplied only through the combustion products, since the obstacles to the diffusion of nitrogen counter to the combustion front are considerable. In this case we observe only one combustion front which travels with deceleration and, after traveling about 1 cm, stops. However, in certain conditions it is not quenched and it is possible to observe a splitting effect ($p_{N_2} \geq 60$ atm). From the bright primary front there emerges a dull front of γ-Ta_2N_{hex} formation which descends at an accelerating rate. This occurs because the counterflow of nitrogen is sufficient to ensure self-propagation. The splitting of the combustion front is illustrated in Fig. 6.

Effect of Diluting the Tantalum with End Product. In synthesizing high-melting compounds, to reduce the combustion temperature, end products are introduced into the starting mixture. We decided to investigate the mechanism of action of this additive under our experimental conditions, using specimens 4 cm long with open ends. Into the starting tantalum powder we introduced a mixture of γ-Ta_2N_{hex} and solid solution of nitrogen in tantalum, as formed during the passage of the first combustion front, and, moreover, δ-TaN_{cub}. The weight of additive varied from 0 to 30%.

The dependence of the nitrogen content of samples taken from the middle of the burnt specimens on the amount of mixture (γ-Ta_2N_{hex} and N_2/Ta solid solution) introduced is shown in Fig. 7 (the amount of nitrogen introduced with the additive has been deducted from the total amount of nitrogen in the samples). Clearly, as the amount of additive increases so does the extent of reaction. The phase composition of the products also varies. Whereas for small amounts of additive the products were two-phase (only γ-Ta_2N_{hex} and solid solution of nitrogen in tantalum), at 30% additive ε-TaN_{hex} was also detected. It should be noted that in this case no second front is observed.

Adding δ-TaN_{cub} also led to an increase in the extent of reaction, δ-TaN_{cub} going over into ε-TaN_{hex} in the combustion front. The average burning rate decreased substantially with increase in the amount of additive. Thus adding end products not only reduces the combustion temperature but also leads to a significant increase in the extent of reaction in the front and, moreover, to a change in the phase composition of the products.

Freezing of End Products in Liquid Argon. This was done in order to study the processes taking place directly in the combustion wave. Both specimens pressed into cylinders (nitrogen supplied through combustion products only) and specimens open at both ends were used; the reactions were frozen in liquid argon either before the front had stopped (first case) or before it had reached the bottom of the specimen (second case). Chemical and x-ray phase analyses of the frozen combustion products in the cylinders gave results that coincided almost completely with those reproduced in Fig. 4.

Analysis of the frozen combustion products of tantalum pressed into tubes showed that near the arrested combustion front in a layer about 3 mm thick only a solid solution of nitrogen in tantalum of average composition $TaN_{\sim 0.04}$ was present. In the combustion front there is a sharp increase in the extent of reaction and the product becomes two-phase (γ-Ta_2N_{hex} and solid solution of nitrogen in tantalum were detected). Then the results completely coincide with those reproduced in Fig. 5 (right side of curve).

It was considered especially important to be able to freeze the specimens at high nitrogen pressures. However, since the tubes were 20 cm long and the reaction space limited, freezing in liquid argon was impractical; accordingly the combustion front was arrested by producing a sharp fall in pressure. The experiments were carried out at $p_{N_2} \geq 500$ atm.

As a result of the sharp pressure drop in the pores of the specimen and the reactor, unburnt tantalum powder was ejected from the tube. Analyses of the burnt part (sintered) showed that the combustion product was single-phase (δ-TaN_{cub}), and the nitrogen content of samples taken at different distances from the arrested front was the same, which coincides with the results of the analysis of unfrozen specimens.

Discussion of the Results

As follows from [2-6], the laws of combustion depend essentially on the amount of nitrogen in the specimen pores. At low nitrogen pressures there is not enough gas in the pores to support self-propagating combustion. Accordingly, it must be supplied to the combustion zone hydrodynamically, by diffusion through the pores as a result of the pressure drop created by the absorption of nitrogen in the front.

As the pressure increases, so does the amount of nitrogen in the pores, and it may become sufficient to support combustion. In Fig. 8 we have plotted the calculated pressure dependence of the possible extent of reaction due to pore nitrogen alone for a temperature of 298°K and a specimen relative density $\Delta = 0.2$ in accordance with the data of [10, 11]. A comparison of Figs. 3 and 8 reveals that at low pressures the extent of reaction is greater than that possible according to the calculations and hence that in this case too nitrogen is supplied to the reaction zone by diffusion.

It is clear from Figs. 1 and 3 that when nitrogen is supplied only through the unburnt part of the specimen the burning rate and the extent of reaction depend essentially on the distance to the open end. This is because as the distance decreases the obstacles to the diffusion of nitrogen are reduced and the rate of supply of nitrogen to the front increases, leading to an increase in the extent of reaction and hence to heat release and a faster burning rate. Thus, the rate of diffusion of nitrogen through the unburnt part of the specimen limits the combustion wave propagation process.

The extent of reaction in the combustion front is low (Fig. 3), but introducing tantalum nitride into the starting powder leads to a considerable increase in the nitrogen content of the products (Fig. 7), and at 30% concentration ε-TaN_{hex}, the end product of combustion, is already beginning to be formed in the combustion front. Since introducing nitride should not affect the diffusion properties of the specimens, this result can be interpreted as follows. When an inert additive is introduced, part of the heat is expended on heating it to the combustion temperature. The burning rate falls, but the extent of reaction increases and the additional heat release makes up for the heat losses.

This result is in good agreement with the data of [4-6] and confirms the detected combustion regimes with incomplete and complete reaction, as well as the absence of collapse of combustion due to heat losses in the incomplete reaction regime.

As shown in [6], when nitrogen is supplied through the combustion products the conversion of metal to nitride in the combustion front must always be complete. Physically, this is because gas will not be supplied to the combustion front until the reaction behind the front ceases, which is possible only when conversion is complete, since the pressure behind the combustion front $p_k > 0$. (The condition for cessation of the reaction is $p_k (1 - m_k) = 0$.) It is clear from Fig. 4 that up to the point at which the visible combustion front stops the extent of reaction is complete, but ahead of the combustion front a partial reaction is also observed, apparently due to nitrogen in the pores of the starting metal.

In this case the average burning rate is substantially lower than for a counterflow of nitrogen. This is attributable to a considerable decrease in the density ofthe gas supplied to the combustion zone since it passes through pores heated to the combustion temperature. If the rate of supply of nitrogen is significantly reduced, the heat released is insufficient to cover the heat losses and therefore the metal ceases to burn.

The combustion of nonmelting porous metal specimens is accompanied by a substantial increase in the degree of nitridation after passage of the combustion wave [2, 3, 7]. In our experiments afterburning occurred only at low pressures and in the presence of a counterflow of nitrogen and was expressed in the form of second and reverse fronts which formed when conversion in the combustion zone was incomplete.

Increased pressure sharply increases the nitrogen content of the pores, which leads to an increase in the extent of reaction in the front and hence in the burning rate (Fig. 2). At $p_{N_2} \geq 500$ atm the combustion regime becomes kinetic. The rate of nitrogen supply ceases to limit the combustion wave propagation velocity and the nitrogen in the pores is sufficient for complete combustion, so that the conditions of nitrogen supply do not affect the burning laws. In this case the burning rate is steady, which is consistent with the data of [6]. The decrease in burning rate with further increase in pressure is evidently associated with increased heat losses.

At low pressures the phased nature of the tantalum – nitrogen reaction is clearly expressed. As freezing showed, in the heating zone the nitrogen dissolves in the tantalum to form a solid solution. This phase is exothermic, but the heat released does not exceed 2 kcal/mole [12]; accordingly the reaction cannot travel independently through the specimen in the form of a combustion wave. The propagation of this phase is controlled by the heat flows from the combustion zone in which the highly exothermic reaction of $\gamma\text{-Ta}_2\text{N}_{\text{hex}}$ formation takes place, with an enthalpy of formation $\Delta H^0_{298} = -65.2 \pm 0.9$ kcal/mole [13]. The third, also exothermic phase involves the formation of $\varepsilon\text{-TaN}_{\text{hex}}$ in the afterburning wave in accordance with the equation [13]

$$\text{Ta}_2\text{N}+1/2\text{N}_2=2\text{TaN}+55.4 \text{ kcal/mole;}$$

accordingly the afterburning front is characterized by intense luminosity. In the afterburning zone a fourth phase is also observed – the endothermic transition from $\varepsilon\text{-TaN}_{\text{hex}}$ to $\delta\text{-TaN}_{\text{cub}}$, the heat of transition being $Q = 5.3$ kcal/mole [13]. This phase occurs because $\delta\text{-TaN}_{\text{cub}}$ is thermodynamically stable only at the high temperature developed during combustion and at elevated pressure [14]. Upon slow cooling of the specimens (annealing) $\delta\text{-TaN}_{\text{cub}}$ should go over into hexagonal ε-TaN, but in the experiments this transition was not observed, evidently owing to the rapid cooling that actually occurred in the freezing process.

Thus, in the diffusion regime the tantalum – nitrogen reaction takes place in four successive phases, the same sequence being observed when the nitrogen is supplied through the unburnt part of the specimen and when it is supplied through the combustion products (Figs. 3 and 4).

In conclusion we note that the experimental data on the laws of diffusion burning are in good agreement with the theoretical results of [4-6]. Moreover, the method employed makes it possible not only to avoid the difficulties associated with studying the combustion mechanism of specimens with an exposed lateral surface but also, given suitable conditions, to isolate the nitride $\gamma\text{-Ta}_2\text{N}_{\text{hex}}$, which extends the range of compounds obtainable by the self-propagating high-temperature synthesis (SHS) method.

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