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# Solid-flame: Experimental validation

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ABSTRACT

The tantalum–carbon reactive system possesses a high energy of reaction with an adiabatic combustion temperature of 2743 K, which is significantly below the melting points of the reactants, as well as any intermediate phases and final products. It was suggested that a combustion wave could propagate in Ta+C mixtures solely owing to a solid–solid reaction. However, this combustion process has never been shown to occur without gas-assisted transport. Here, we report preparation of highly pure and pore-free Ta/C composite particles, which were used for experimental validation of the solid-flame. Preparation of these composite particles involves short term high-energy ball milling (HEBM) of tantalum and carbon powders. High-resolution microscopy coupled with three-dimensional reconstruction techniques were used to characterize the volume nanostructure of mechanically fabricated composite particles. It was quantitatively shown that the particles have nano-scale mixing of the reagents and possess high contact surface area between tantalum and carbon. Experiments revealed that the ignition temperature of as fabricated composite particles is 1243 ± 15 K and maximum combustion temperature was shown to be 2487 ± 50 K, which is well below any possible solid–liquid transitions. Utilizing results obtained with composite particles prepared under different HEBM conditions, it is shown that carbon diffusion through the tantalum grain boundaries and subsequent formation of a Ta(C) solid solution defines low temperature ignition of mechanically fabricated particles. The high surface area contact between the Ta and C nano-scale reagents allows the reaction to propagate in a self-sustained manner, owing solely to a solid-state diffusion mechanism.



## 1. Introduction

Combustion synthesis (CS) or Self-Propagating High Temperature Synthesis (SHS) is a well-established non-traditional energy saving approach to produce a variety of materials, including metals and their alloys, ceramics and cermets, composites and functionally graded compounds, 2D-crystals, and nano-powders [1–6]. Although CS is attractive for many applications, there are still fundamental issues in solid physics that need to be resolved. One of these issues is the concept of a solid-flame [7]. This came about in 1967, when a group of Russian scientists from the Semenov Institute of Chemical Physics, headed by Prof. A. Merzhanov, discovered a wave localization phenomena for solid state self-propagating reactions [8], or in modern terms the *solid flame*. The fundamental basis for this phenomenon is the following: (i) in some exothermic reactive mixtures (e.g. Ta–C and Mo–B), the adiabatic combustion temperature, while being high, is still well below the melting points of the precursors, any intermediates, and final products (see Fig. 1 for the Ta–C system); (ii) the amount of equilibrium gas phase products in these systems are negligibly small; (iii) it was experimentally shown that a combustion wave may propagate in a self-sustained manner along such reactive heterogeneous media with velocities ranging from 0.1–1 cm/s. Thus, it was suggested that a solid-state reaction, localized in the combustion front, may self-propagate in a heterogeneous gasless system, which leads to the concept of a solid flame.

From the standpoint of conventional combustion, a solid flame is enigmatic, because it is hard to believe that solely solid-state diffusion may define the self-sustaining nature of the combustion process. It is a prevalent opinion that self-propagating combustion processes, such as metallothermic reactions, exist due to relatively fast mass transport in the liquid phase (diffusion and convection); therefore, melting of at least one component in the system is considered as a necessary condition for combustion. Recently this requirement was even announced as a "new criterion" for sustainability of the combustion reaction: "*adiabatic temperature … must be high enough* to melt the lower melting point component" [9]. On the other hand, the regularities of combustion in Ta+C mixtures were studied by Shkiro

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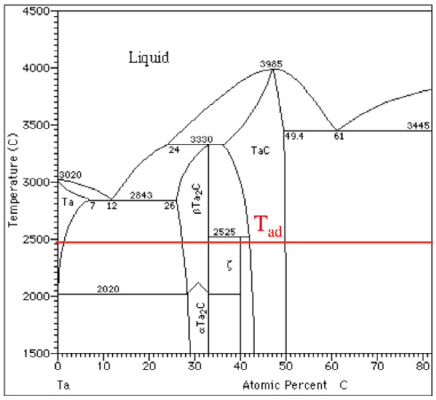


**Fig. 1.** Phase diagram of the Ta+C system. The adiabatic temperature is indicated. The maximum possible temperature is well below any eutectic or phase transition point.

and co-authors assuming that the reaction proceeds completely in the solid state [10]. It was shown that the combustion wave in the Ta–C system can propagate in the pulsating mode at temperatures below the lowest melting or eutectic point. More careful experimental investigation of the combustion mechanism revealed, however, a gas-transport stage in the combustion reaction for this system [11]. In that article, based on detailed investigation of the structural transformations taking place in the combustion front, it was shown that impurities enhance mass-transport in the Ta–C system. Investigation of the microstructural transformations in the quenched combustion wave revealed that:

- The tantalum carbide (TaC) crystals that formed in the leading zone of the reaction front have columnar morphology and uniformly cover the particle surface, despite that, in the initial mixture, the reagents have only point contacts;
- The final combustion product consists of globular TaC particles.

These structural transformations led to the hypothesis that the existence of a gas phase and melt leads to enhanced reagent transport, and consequent product formation in this system. These phases form due to the impurities present in the initial reagents, such as oxygen, in a form of oxide film on the surface of the metal particles, and iron, introduced into the system during the mixing process. A variety of model experiments confirmed this hypothesis; small amounts of iron, distributed on the tantalum surface, accelerate combustion along with gas phase mass-transfer of carbon through the Boudouar-Bell cycle, which reduces the tantalum oxide film and leads to the formation of columnar structures on the surface of the metal particles. In 2001 the term "*catalytically assisted combustion synthesis of tantalum carbide*" has been introduced by Kim and Wooldridge [12]. They indicated that the presence of iodine vapor and carbon dioxide significantly enhances the combustion synthesis process, leading to higher conversion efficiencies and influencing the product microstructure. There are also reports by Kashireninov et al. [13] and Egishyan et al. [14] on the leading role of gas phase reactions during combustion in the other thermodynamically solid flame system, i.e. the Mo–B mixture.

Thus the question still remains: can the solid-flame be accomplished in its pure form? A.G. Merzhanov suggested a term "*ideal solid flame*" for a combustion processes where all gas and liquid phases are absent, as opposed to real solid flames where impurities can promote the process though formation of small amounts of gases or liquids [7]. Till now, the existence of the ideal solid flame has not been proven. In order to assert the ideal solid flame in the Ta–C system, one has to form a pore-free media of tantalum and carbon, with no impurities that have melting points below the adiabatic combustion temperature. In this case, there is no space (pore-free) for gas transport and the melt cannot be formed in the combustion wave. In order to create such a media, advanced processing techniques must be utilized.

Short term (<10 min) high energy ball milling (HEBM) has received considerable attention in recent years as a method for fabrication of composite nano-structured reactive particles with oxide-free surface contact between solid reactants [15–18]. The mixture of powders, which initially only have point contact with each other, is subjected to the intensive (acceleration in the range 20–300 G) mechanical treatment under an inert atmosphere in a ceramic ($ZrO_2$) milling jar. As a result, new, typically pore-free, composite particles are formed, which involve both elements, mixed on the nano-level with essentially oxygen-free contact surfaces. It is also important, as was shown for many systems, such structural transformations significantly decrease the reaction onset (ignition) temperature and accelerate the combustion front propagation [19,20].

In this work we used short term (4 min) HEBM for preparation of composite Ta/C particles. The internal nano-structure of these particles was investigated and characterized using 3D-reconstruction techniques. The ignition and combustion parameters of the reactive media were thoroughly studied. Analysis of the obtained data allows us to conclude that the solid flame phenomenon can be accomplished in such a system. To support this conclusion, a simple model, based solely on solid-state diffusion, is also proposed and discussed.

## 2. Experiment

### 2.1. Initial reactants

Tantalum powder (Materion Advanced Chemicals, 99.9% pure, < 44 μm) and carbon lampblack (Fisher Scientific, 99% pure) were used as precursors. EDS analysis reveals less than 1 wt. % of oxygen in the initial powder mixture. The microstructures of these powders are shown in Fig. 2. It can be seen that the metal particle sizes range from 5 to 20 μm (Fig. 2a) and are comprised of irregular planar geometries (Fig. 2b), while carbon lampblack particles (Fig. 2c) are agglomerations of much smaller (<2 μm) spherical carbon particulates (Fig. 2d).

### 2.2. High energy ball milling

HEBM was performed by a PM100 (Retsch, Germany) planetary ball mill in a 500 mL zirconium oxide jar with 1 mm balls of the same

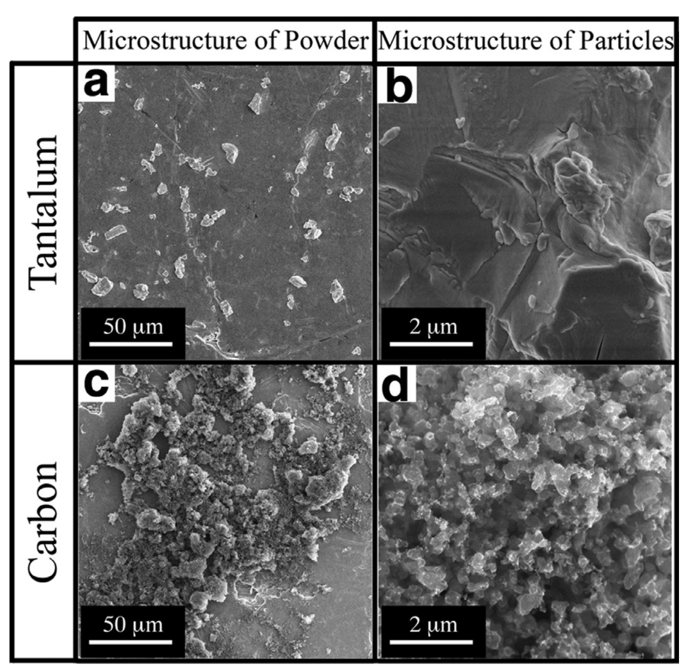


**Fig. 2.** SEM images of the initial reactant morphology. The tantalum is plate-like and flat, between 5 and 40 μm. The carbon is amorphous and roughly spherical, consisting of large agglomerations of particles, individually under 2 μm.

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