High-temperature reactive melt spreading: Experimental modeling of SHS reactions

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Abstract. Initial stages of high-temperature spreading and inreaction of molten droplets with solid substrates were experimentally investigated in the systems Ti–C and Nb–B. Thin layer of solid product (carbide, boride) crystalline grains forms immediately in the spreading frontier, while the melt infiltrates through nano-scale gaps between grains. The formation of a continuous layer of oxidation- and wear-resistant solid refractory (\(~3000^\circ C\)) product can be utilized for coating protection of refractory metals and carbon materials, as well as in high-temperature joining of carbon materials via a thin layer of titanium carbide.

1. Introduction

Reactive spreading of melts plays a key role in the mechanism of self-propagating high-temperature synthesis (SHS), especially in systems combining melting and non-melting reagents. The effect of capillary spreading was first observed in the Ti–C system [1] and then experimentally and theoretically explored in [2–4]. For different ratios of melting points of metal to non-metal, different scenarios of the spreading process can be expected to occur. For instance, in metal–carbon systems a metal melt spreads over the surface of solid carbon particles to yield carbide grains. Recently, we have found that melted Ti spreads over the carbon surface through the channels formed between TiC grains [5]. Less studied are the systems (such as Nb–B, Mo–B, Ti–Si) in which the melting point of non-metal is lower than that of metal, so that in this case non-melt has to react with solid particles of metallic reagent. Previously, some general features of the spreading process were explored in a particle–foil approximation for Nb–B [6] and Ti–Si [7] systems, although some subtle details remain unclear. Finally, there exist some systems (e.g. Ni–Al) in which both constituent components are low-melting and, as a result, SHS reactions take place between two melted reagents.

In this work, we report on comparative analysis of reactive spreading of melted metal and nonmetal reagents over the surface of solid reagent.

2. Experimental

The particles of low-melting reagent (B, Ti) were placed on thin substrate of high-melting reagent (Nb, C, respectively). The latter was heated (at $10^{-3}$ Pa) by a pulse of electric current (pulse duration between 0.5 and several seconds) to a temperature above the melting point of particles but below that of substrate.
The process was recorded with a high-speed video camera. Combustion products were characterized by SEM, STEM, and TEM.

3. Results and discussion

3.1. Nb–B System
Due to melting boron crystals on the surface of Nb foil, on the spread boron particles we observed the craters covered with finely dispersed reaction product (figure 1). According the results of EDS analysis, the product contains B, Nb and small admixtures of O, N, and C. Using focused ion beams, we managed to cut out thin plates oriented normally to the direction of spread propagation and used them in TEM studies (figure 2).

As can be inferred from figure 2, the Nb substrate gradually dissolved on the perimeter of spreading. The dissolution zone is about 5 \( \mu \)m in its width, while the depth of metal erosion makes a value of 3–4 \( \mu \)m (figure 2). The product layer was formed by 1-\( \mu \)m crystals of hexagonal NbB\(_2\). No unreacted boron (as well as other boride phases) was detected in between the product grains. The absence of other borides can be explained by the fact that temperature of the melt was higher than crystallization temperatures of all the borides in the Nb–B system. Melted boron spread over the surface of NbB\(_2\) layer and transformed to diboride on the perimeter of spreading.

3.2. Ti–C System
The spread of melted 100-\( \mu \)m Ti particle over the graphite surface was found to proceed in three stages. The first one is accomplished in a time period of about 50 ms (figure 3). It can be assumed that, at this
stage, spreading rate $V$ is controlled only by the rate of Ti melting. This is followed by a slow growth in diameter of the spreading spot ($D$) up to $t = 500$ ms (figure 3). Finally, the spreading area (spot) loses its rounded shape due to Ti spread along surface imperfections. The process of spreading decelerates and can last even for several seconds until all Ti transforms into TiC crystalline grains. Initially $V$ has a value of 1.8 cm/s (in some experimental runs even 6–7 cm/s), which is close to burning velocity of powdered Ti–C mixtures. At the second stage, spreading rate decreases down to 1–2 mm/s.

![Figure 3](image3.png)

**Figure 3.** Diameter of spreading Ti spot ($D$) and its spreading rate ($V$) as a function of time $t$.

Figure 4 illustrates the fine structure of circular reaction zone. Platelet TiC grains 2–3 μm in size and ~ 0.5 μm thick are seen (figure 4a) to arise directly at the contact surface. There is a 100–150 nm gap between the grains through which Ti melt can infiltrate to the perimeter of spreading. The layer-structured grains are oriented along the substrate surface. The lowest TiC layer with a thickness of below 100 nm is extended and acts as a base for the growth of new carbide grains. This layer plays the role of ‘leading’ structural component in the process of Ti propagation over graphite: ahead of this layer, no Ti on the graphite surface was detected. Meanwhile, the results of atomic-force microscopy and profilometry have revealed the presence in the substrate, ahead of spreading perimeter, of some cave several μm wide and about 300 nm deep, which can be tentatively associated with dissolution of carbon in Ti melt.

![Figure 4](image4.png)

**Figure 4.** Fine structure of reaction zone (SAFM image).
The above results allow us to suggest the following mechanism for interaction between Ti and C in the conditions under consideration. The Ti melt formed at the area of contact between reagents is spread over the surface of solid carbon material and yields micron and sub-micron platelet TiC crystals. The occurrence of crystallization clearly indicates that the Ti melt saturated with carbon due to dissolution of carbon in melted titanium. In the contact area, the carbide grains form an island structure with a network of straits around 100 nm wide, through which melt spreading is effectuated. Initially, melt is spreading over the framework on newly formed TiC grains with open porosity. Despite the formation of solid product, direct contact between melted titanium and solid carbon still remains effective, which ensures a high rate of the reaction. Apparently, such a mechanism plays a key role in SHS of refractory compounds and materials.

When the Ti particle was placed on the surface of laminated carbon (pyrographite), it was found that interaction of Ti droplet with a substrate of pyrographite lead to the splitting of the substrate into thin layers (figure 5) that were drawn into the Ti droplet to form TiC grains. At this, one of these layers is seen to crawl over the droplet surface. This phenomenon can be used for creating textured microstructures and multilayer graphene sheets.

![Figure 5. Disintegration of pyrographite and carbidization of nanolayers.](image)

4. Conclusions
The formation of a continuous layer of oxidation- and wear-resistant solid refractory (~3000°C) product can be utilized in deposition of protective layers onto the surface of refractory metals and carbon materials, as well as in high-temperature joining of carbon materials via a thin layer of titanium carbide.

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