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In situ characterisation of mechanically-induced self-propagating reactions

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Transparent quartz vials were employed for a direct viewing of ignition and propagation phenomena in combustion-like reactions under milling. Combustion temperatures were measured from infrared light emission by two-colours pyrometers. Such a methodological approach allowed one the *in situ* characterisation of the self-propagating behaviour of a variety of carbides and silicides. Experimental combustion temperatures close to the theoretically calculated adiabatic ones were observed for the reaction which goes to completion within millisecond period. © *2004 Kluwer Academic Publishers*

1. Introduction

It is well known that when a highly exothermic chemical system is mechanically treated by Ball Milling (BM), a combustion-like reaction can take place, resulting in a very fast formation of the products. This process is generally referred to as Mechanically-induced Self-propagating Reaction (MSR) [1, 2] or Explosive Mechanochemical Synthesis (EMS) [3].

The spontaneous ignition of the MSR process occurs related to a certain stage of the microstructural refinement of the reactant phases and to an increase in the structural disorder. However, the reasons which determine the ignition of the reaction and its propagation mode and rate are still scarcely understood. This is in part due to the fact that the conventional mechanochemical reactors are made in steel which does not permit the direct observation of the process. As a consequence, the reaction ignition can be only noticed from a sudden increase in the vial temperature, due to the reaction heat.

In the past years, very few authors employed transparent mechanochemical reactors to remove these restrictions. Butyagin *et al.* were the first to employ a quartz apparatus to measure the excitation spectra and to monitor the luminescence phenomena in the course of the milling treatment [4, 5]. Courtney *et al.* modified an attritor mill with a Plexiglas container in order to study its milling dynamics [6]. Koch *et al.* employed a transparent Lucite vial in a Spex Mixer/Mill mod. 8000 to evaluate impact frequency and collision energy [7].

Recently, we also conceived a mechanochemical reactor in transparent quartz to monitor the occurrence of the MSR reaction by means of video recording systems and infrared thermometers [8, 9].

In this paper we provide the details of this experimental methodology and the results of its application to the Ti-C, Ta-C and Ti-Si systems.

2. Materials and methods

The trials were performed by using either a commercial Spex Mixer/Mill mod. 8000 or a prototype uniaxial vibro-mill which is characterised by a simpler motion and allows one a continuous registration of the temperatures by means of the infrared thermometers [8, 9].

The transparent mechanochemical reactors, shown in Fig. 1, were made of quartz by the QSIL-Quarzschmelze Ilmenen GmbH—Germany. The fused quartz was chosen because of its good transmittance properties—it permits to monitor the MSR evolution with suitable sensors, coupled with good mechanical properties in a wide temperature range. An extremely low coefficient of thermal expansion (5.5×10^{-7} mm/K between 20–320°C) ensures a high thermal shock resistance with a high softening point (1993 K). These properties make the quartz vials resistant to the grinding action of the balls and powder particles and to the high temperatures reached during the MSR reactions. Finally, the fused quartz is chemically inert and impermeable for most gases.

A MotionScope 8000 S Color (Redlake Imaging, Morgan Hill, CA) and a SpeedCam Mod. 2000 Black and White (Weinberger Deutschland GmbH,

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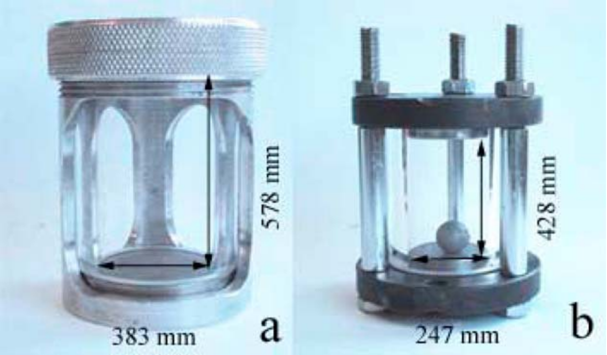

Figure 1 Quartz vial employed in the Spex mill (a) and Vibro mill (b). Vial (a) has the inner dimensions equal to the standard Spex vial.

Karlsruhe G), permit to record the MSR reaction up to a rate of 8000 frame/s.

The combustion temperatures were measured by two high-speed infrared thermometers (Land System 4 Fibroptic—Land Infrared Ltd., England) operating between 873–1873 K and 1273–2873 K.

The infrared thermometers are connected to a PC-based data acquisition system equipped with a NI PCI–6023E plug in board able to record up to 200 kHz. A software was suitably developed to control and synchronize video and temperature recording. The videos were analyzed with a Redlake MotionScope PCI 2 2.20 software supplied by Redlake Imaging.

Powders of Ti (ALFA-200 mesh, 99.5%), Ta (ALFA-325 mesh, 99.97% 50 ppm Nb), C graphite (ALFA-325 mesh, 99.5%) and Si (ALFA-325 mesh, 99.5%) were used.

Preliminary tests were performed with a stainless steel vial, in order to measure the ignition time, t_{ig}, from the abrupt increase of the temperature, see Fig. 2. In subsequent trials the reactant powders were treated in the steel vial for a time close to the ignition time, then transferred in the quartz reactor and subjected to further mechanical treatment up to the combustion.

All the handling procedures were performed within a glove-box under inert atmosphere.

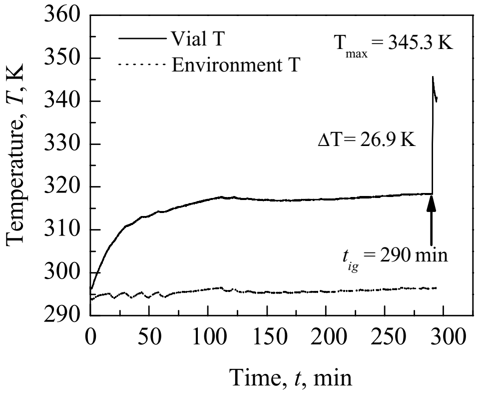

Figure 2 Vial temperature as a function of time during the milling of Ta:C = 50:50. The temperature is recorded with a Pt resistance thermometer (Pt100) fixed on the external vial surface. The ignition is marked by the sudden increase of the vial temperature.

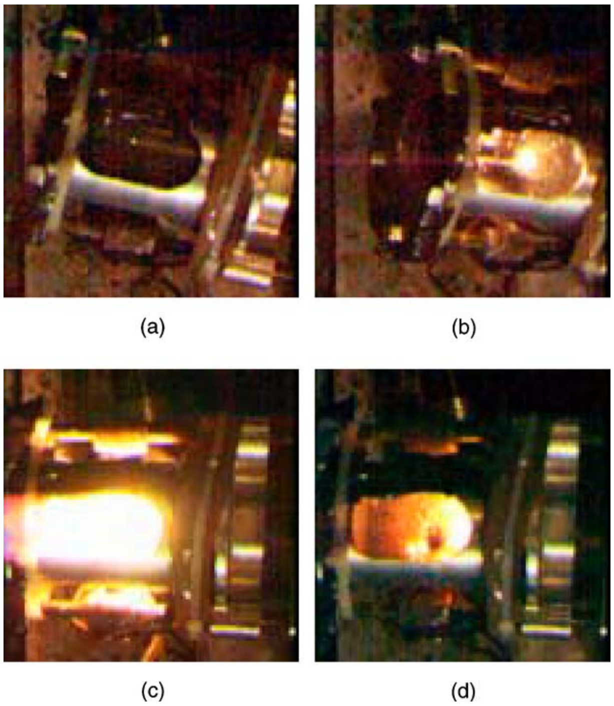

Figure 3 High-speed image sequence of the reaction of the Ti:Si = 5:4 mixture in the Spex mill. Frames refer to some of the ignition events and to the maximum brightness at the completion of the reaction. The motion of the Spex mill occurs along the vial axis.

3. Results and discussion

A few frames of a typical MSR reaction carried out in the quartz reactor are shown in Fig. 3. The frames refer to an experimental trial performed on the Spex mill and illustrate the combustive synthesis of a Ti:Si = 5:4 mixture. The careful inspection of the recorded video suggests that, at least in the case of the Spex mill, the reaction is likely to be ignited either along the vial wall, in connection with the sliding of the ball on it causing attrition or at the impact of the ball against the vial bases.

The high temperature reached by the hot particles in the observed bright spots can then induce the ignition of the reaction in the neighbouring particles. However, according to the acquired frames rarely the reaction starts following the first burning particles. We observed, indeed, that the formation of the spots is often followed by their rapid disappearance without any further reaction. This suggests that the true ignition and reaction propagation actually occurs only when the powder in the mixture has reached a suitable degree of structural deformation during the mechanical mixing.

After ignition, the reaction propagates throughout the whole mass of powder because of the continuous and violent scatter of the particles due to the reciprocating vial motion. A frame concerning the propagation process is shown in Fig. 3b. At this level the reaction propagates even if the mechanical processing is interrupted.

For the present case, as shown in Fig. 3c, the reaction reaches the maximum brightness and therefore the maximum rate and combustion temperature after a few hundred of ms.

After that the reactant powders cool as shown in Fig. 3d.

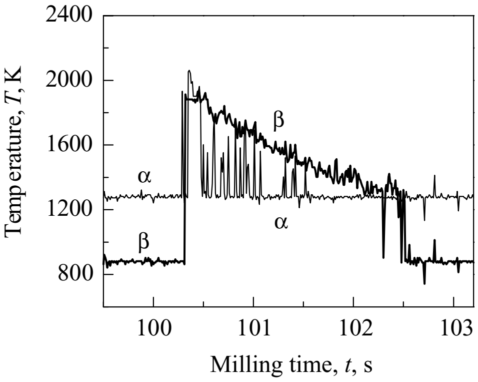

Figure 4 Optical measurement of the temperature inside the quartz vial during the milling of a Ti:Si = 5:4 powder mixture. Traces refer to the powder temperature as registered by two infrared thermometers operating at (α) 1273–2873 K and (β) 873–1873 K.

The data concerning the temperature acquisition are reported in Fig. 4. To avoid excessive disturbance due to the vial motion, as in the case of the Spex mill, the reaction has been performed on the prototype vibrating grinder. Rapid oscillations in the pyrometer readings are simply due to the rapid motion of the burning powders, which periodically leave the visual fields of the pyrometer sensors. A maximum temperature of 2063 K, slightly lower than the calculated adiabatic one of 2193 K, was registered. It can be noted that this temperature is well above the melting temperatures of the reactants.

During the course of the cooling process it becomes possible to track the motion of glowing ball. As detailed elsewhere [10], we took advantage of this to evaluate the ball and vial velocity at the impact.

We move now to the Ta:C = 50:50 system. Results here refer to trials carried out in the vibro mill. The frames reported in Fig. 5 relate directly to the temperature readings as registered by the two pyrometers. In the frame (a) a bright spot is clearly visible on the vial base and it suggests that the ignition starts on the vial bases when the vibrating grinder is used. As in the previous case, this first attempt extinguishes after a few ms without inducing any further reaction. Hot particles reappear on the same base after 731 ms. This particle cluster is now able to ignite the reaction which propagates very fast. The maximum brightness, frame (d), is reached after about 36 ms, a value one order of magnitude lower than the one of 360 ms observed in the case of the Ti_5Si_4 system. In correspondence to the maximum brightness, the maximum combustion temperature of 2870 K is also reached, as shown in Fig. 5. Once again, the combustion temperature is slightly below the adiabatic one, equal to 2901 K. In this case, however, it is considerably lower than the melting temperatures of the reactants. However, the main point here is that the reaction occurs well below the melting temperature of the reactants and as a consequence, the reaction propagates with a solid-solid diffusion mechanism. The frame (e) pertains to the cooling process.

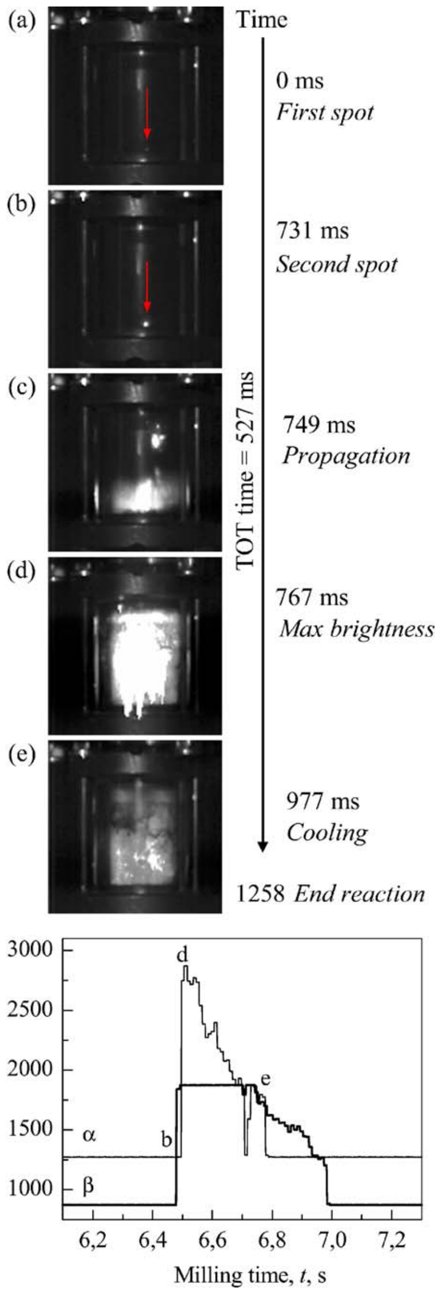

Figure 5 High-speed image sequence of the reaction of the Ta:C = 50:50 mixture in the Vibro-mill coupled with the related temperature recording obtained by the infrared thermometers.

Table I summarizes the experimental combustion temperatures for several systems investigated with the methods described above [8, 9]. For the sake of comparison, we report the corresponding adiabatic temperatures. It is worth noting that the combustion temperatures registered by the pyrometers are invariably close to the calculated adiabatic temperatures.

TABLE I The experimental combustion temperatures and the calculated adiabatic temperatures for the various systems investigated

Chemical system	Adiabatic temperature, T_{ad} (K)	Combustion temperature, T_c (K)
Ti_5Si_3	2550	2420
TiSi	2370	1818
Ti_5Si_4	2193	2063
$TiSi_2$	1829	1613
$Ti_{70}C_{30}$	1991	2183
$Ti_{60}C_{40}$	2614	2773
$Ti_{50}C_{50}$	3206	>2873
$Ta_{50}C_{50}$	2901	2870

4. Conclusions

The methodology we developed to monitor the occurrence of the MSRs represents a valuable tool to deepen our knowledge in this particular field. We have been able to gain the qualitative features of the ignition process under mechanical processing conditions. Ignition relates to the formation of initial burning particles as detectable in the video snapshots as bright spots. It also appears that reaction propagates when the reactant powders have reached a characteristic level of microstructural refinement. The direct view technique allows one to measure the propagation times which proved characteristic of each chemical system.

An important point is the direct evaluation of the combustion temperature of the reacting systems. We obtained a clear evidence of the melting of at least one of the reactants in all the systems investigated, Ta-C excepted. In this case the reaction should proceed according to the solid-solid mechanism already observed under conventional SHS (Self-sustaining High-temperature Synthesis) conditions. It is therefore possible to surmise that once ignited, the MSRs proceed according to the same mechanisms of the conventional SHS reactions.

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