



Effects of additives on the synthesis of $\text{TiC}_x\text{N}_{1-x}$ by a solid-gas mechanically induced self-sustaining reaction



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ABSTRACT

The synthesis of $\text{TiC}_x\text{N}_{1-x}$ from Ti/C mixtures in a N_2 atmosphere performed in a high-energy planetary mill was used as example to study the influence of the use of additives in mechanically induced self-sustaining reaction (MSR) processes. In particular, the effect of the addition of TiN, TiC, Si_3N_4 and SiC was analyzed. The self-sustaining reaction was extinguished when additive contents of 50, 40, 40 and 30 wt% for TiN, TiC, Si_3N_4 and SiC, respectively, were employed. These additives cannot be regarded as real inert since they served as an extra solid source for nitrogen and carbon, modifying the final stoichiometry of the $\text{TiC}_x\text{N}_{1-x}$ phase. The adiabatic temperature (T_{ad}) determined for the mixtures with no MSR effect was well above the empirical limit value of 1800 K adopted as criterion for the occurrence of the self-propagating high-temperature synthesis (SHS) process. The ignition time (t_{ig}) of the MSR process was practically invariant for low additive contents (approximately 50 min) and tended to increase up to maximum values of 85–95 min for the larger additive contents.

1. Introduction

Combustion processes have been widely employed to synthesize a great variety of technological materials as they have the advantages of short processing time, low energy consumption and affordable cost, which are especially interesting for producing refractory compounds [1]. These processes are based on extremely exothermic reactions, so that when they are initiated, the heat released by them, generating a combustion wave, is the main energy source for the conversion of the reactants into products. As a rule of thumb, it is accepted that a combustion process may occur if the empirical criterion of an adiabatic temperature (T_{ad}) greater than 1800 K is met for the exothermic reaction. This thermodynamic parameter is defined as the maximum temperature reached by the products under adiabatic conditions as a result of the reaction heat.

The ignition of the combustion process can start by applying thermal or mechanical energy. In the former case (the most usual), there are two main methods; the self-propagating high-temperature synthesis (SHS) [2] and the thermal explosion (TE) [3]. The difference between these two combustion modes is that in SHS, ignition is produced by a heat source at one end of the reactant compact (at the surface) and the propagating front travels through the bulk sample, while in TE, a volumetric heating is performed so that ignition occurs

simultaneously throughout the whole compact. The temperature at which the reactant mixture is ignited is called the ignition temperature (T_{ig}). This temperature is considerably lower than the combustion temperature (T_{c}), which is the maximum temperature reached at the propagating front that is in turn slightly lower than T_{ad} due to heat loss phenomena.

On the other hand, if the combustion is induced by high energy milling (mechanical energy), the method is referred to as a mechanically induced self-sustaining reaction (MSR) [4]. In MSR, ignition does not happen at the beginning of the milling process, but after a critical milling time called the ignition time (t_{ig}). During the milling time prior to ignition, the activation of reactants takes place, during which mixing, size reduction and creation of defects occur. When the reactant mixture is sufficiently activated and reactive, the subsequent ball impacts induce the onset of the mechanochemical reaction and an increase in the conversion rate. In highly exothermic systems, the heat released by this incipient mechanochemical reaction is capable of initiating the combustion reaction, which rapidly propagates through the powder charge transforming the reactants into products. t_{ig} , which is the equivalent parameter to T_{ig} in the thermally-initiated processes, depends not only on the reactant system, but also strongly on the experimental milling conditions [5–7].

Despite combustion processes fall into the category of extreme

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chemical reactions [8], characterized by extremely high combustion temperatures, propagation velocities and heating rates, thermally-induced processes (SHS and TE) can be controlled through different process parameters, such as the reactant particle size, the green density of compacts, the preheating temperature (in TE this parameter is always equal to T_{ig}) and the starting stoichiometry, which also includes the use of additives or diluents [9]. In MSR processes, the main controlling experimental parameters that have been studied are the dynamics of the ball motion, which determines the impact energy and the impact frequency, both imposed by the type of mill and the speed of its motion [6,7,10], the ball-to-powder ratio (BPR), which determines the volume of powder trapped during impacts per unit time [11], and the composition of the reactant mixtures [12]. Independently of the combustion process performed, the suitable selection of the experimental conditions is required to obtain a product with the desired morphology and properties.

The addition to the reactant mixture of an inert compound as a diluent is frequently used to control the combustion process. This compound does not contribute to the generation of heat, but absorbs it, which has an effect in decreasing the exothermicity of the reaction, making it less violent since T_c is reduced [13]. The maximum diluent content that can be added to a reactant system is fixed by the extinction of the combustion reaction, i.e., there is no combustion even upon intense initiation. Normally, the diluent is the final product of the combustion reaction [14–16], although in some cases an excess of one of the reactants [17–19] or an independent compound that does not belong to the reactant system [20–22] has also been employed. External diluents are normally used when a composite material is the intended end product and the diluent is one of the constituent phases of the composite [20,21]. Otherwise, the diluent should be properly removed by washing methods after the combustion process [22]. However, the use of external diluents sometimes lead to unexpected products as they may participate in the SHS process by undergoing some kind of physical or chemical modification [23,24].

When T_c diminishes due to the presence of diluents, the microstructure and composition of the product can be modified as the formation of large highly bonded aggregates (self-sintering) and the appearance of molten (or vaporized) phases (reactants or products) can be avoided [14]. Also, as diluents impede a good contact between the product particles during the reaction and the after-burning (once the propagating front has passed) periods, the grain growth is reduced [21]. Sometimes, diluents melt during the combustion process and the grain growth is prevented by creating a protective layer on the particle surface [25]. In other cases, molten diluents may improve the kinetics by allowing the reaction to be completed through dissolution-reprecipitation processes [26]. Besides, the reaction mechanism, the reaction sequence and the formation of intermediates may also be affected by the presence of diluents [27].

Although the use of diluents in thermally-induced processes has been extensively studied, fewer examples can be found in MSR processes [28–34]. In this work, the effects of different additives on the synthesis of titanium carbonitride (TiC_xN_{1-x}) by MSR and the characteristics of the obtained end product were analyzed. The synthesis of TiC_xN_{1-x} from Ti/C mixtures in a N_2 atmosphere is a highly exothermic reaction with high T_{ad} , TiN (4900 K) and TiC (3340 K), and can be accomplished by SHS [35,36] and MSR [37]. In particular, two additives (TiN and TiC) belonging to the Ti–C–N system and two external additives (Si_3N_4 and SiC) were employed. TiC_xN_{1-x} is an important hard material because of an excellent combination of properties, such as high melting point, significant hardness–toughness compromise, thermal conductivity, good chemical oxidation, wear resistance and low electrical resistivity [38]. It is employed for example as cutting tools and for other wear-resistant structural applications [39,40].

2. Experimental procedure

Titanium (Ti) powder (99% purity, < 325 mesh, Strem Chemicals), carbon powder (C) as graphite (11 m^2/g , $Fe \leq 0.4\%$, Merck), titanium nitride (TiN) powder (98% purity, < 325 mesh, Aldrich), titanium carbide (TiC) powder (98% purity, < 325 mesh, Aldrich), silicon nitride (Si_3N_4) powder (99% purity, < 325 mesh, Aldrich), silicon carbide (SiC) powder (99% purity, < 400 mesh, Fluka) and high-purity nitrogen gas (H_2O and $O_2 < 3$ ppm, Air Liquide) were used in this work. Ti/C powder mixtures with an atomic ratio of 1/0.5 and different amounts of additives were milled under a N_2 atmosphere using a planetary ball mill (Pulverisette 7, Fritsch). All milling experiments were conducted using a 45 mL tempered steel vial (67 HRC), 6 g of powder charge, 7 AISI 420C stainless steel balls ($d = 15$ mm and $m = 13.7$ g), a BPR of 16, a spinning rate of 600 rpm and a N_2 pressure of 6 bar. The vial with a special lid was continuously connected to the gas cylinder by a rotating union (model 1005-163-038, Deublin) and a semi-rigid polyamide tube (Legris), allowing working under a constant gas pressure that was monitored during milling by a pressure transducer (AKS, Danfoss) connected to a paperless recorder (Ecograph T RSG30, Endress + Hauser). When the ignition and the spreading of the self-sustaining reaction occurred, the increase in temperature induced the instantaneous increase in the total pressure and a sharp peak appeared in the pressure-time record, from which t_{ig} was determined. Milling was stopped 15 min after ignition. T_{ad} for the different mixtures was determined from the thermodynamic functions of heat capacities and enthalpies of formation and transformation of products [41] according to the methodology shown in [9].

X-ray powder diffraction (XRD) patterns of milled powders were performed on a X'Pert Pro MPD diffractometer (PANalytical) equipped with a graphite diffracted beam monochromator and a solid-state detector (X'Cellerator), using Cu $K\alpha$ radiation (45 kV, 40 mA) over a 2θ -range of 20–120° and a step size of 0.017°, with a counting time of 300 s/step. The lattice parameter of TiC_xN_{1-x} was calculated from the entire set of peaks in the XRD patterns using the Fullprof computer program assuming a cubic symmetry. As TiC_xN_{1-x} is a complete solid solution phase in the TiC–TiN system and its lattice parameter is a linear function of the C and N content that fulfills the Vegard's law [37], the stoichiometry of TiC_xN_{1-x} was estimated from the linear dependence calculated from the following reference diffraction patterns from the PDF-4 + database of the International Centre for Diffraction Data (ICDD): TiN (38–1420), $TiC_{0.3}N_{0.7}$ (42–1488), $TiC_{0.7}N_{0.3}$ (42–1489) and TiC (32–1383).

3. Results and discussion

3.1. Influence of TiN addition

Table 1 shows the results obtained for the milling experiments performed with different amounts of TiN as an additive, in which T_{ad} and t_{ig} values are included. An MSR process was detected up to a

Table 1
Ti/C mixtures milled in 6 bar of N_2 with addition of different TiN amounts. T_{ad} : adiabatic temperature for TiC_xN_{1-x} formation; ν : theoretical percentage of liquid phase at T_{ad} ; t_{ig} : ignition time; a : lattice parameter.

Sample	Additive content, TiN (wt%)	T_{ad} (K)	ν (%)	t_{ig} (min)	a (Å)
0TiN	0	3870	100	50.5	4.299
5TiN	5	3552	100	49	4.294
10TiN	10	3282	97.6	50	4.288
15TiN	15	3282	81.9	52	4.286
20TiN	20	3282	66.0	50	4.284
30TiN	30	3282	33.6	70	4.279
40TiN	40	3223	3.8	85	4.278
50TiN	50	2857	0	No MSR	–

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