MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5227–5230

Role of mechanical activation in SHS synthesis of TiC

F. MAGLIA*
Dipartimento di Chimica fisica, Università di Pavia, V. le Taramelli 16, I-27100 Pavia, Italy
E-mail: filippo.maglia@unipv.it

U. ANSELMI-TAMBURINI
Dipartimento di Chimica fisica, Università di Pavia, V. le Taramelli 16, I-27100 Pavia, Italy;
Department of Chemical Engineering and Materials Science, University of California,
Davis, CA 95616-5294, USA

C. DEIDDA
Dipartimento di Chimica, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy

F. DELOGU
Dipartimento di Ingegneria Chimica e Materiali, Università di Cagliari, Piazza d'Armi,
I-09123, Cagliari, Italy

G. COCCO
Dipartimento di Chimica, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy

Z. A. MUNIR
Department of Chemical Engineering and Materials Science, University of California,
Davis, CA 95616-5294, USA

The effect of the mechanical activation of the reactants on the self-propagating high-temperature synthesis (SHS) of titanium carbide was investigated. The SHS experiments were performed on two compositions, $Ti_{50}C_{50}$ and $Ti_{70}C_{30}$, which define the homogeneity range of the TiC equilibrium carbide. Milling times were progressively increased up to the time at which a combustion-like process ignites spontaneously under milling. The combustion peak temperature, wave velocity, and ignition temperature were markedly influenced by the degree of mechanical activation of the reactants. In particular the ignition temperature was observed to decrease from a temperature corresponding to the melting point of Ti to 500°C. The apparent activation energy for propagation of the combustion wave was also determined ($\sim$100 $kJ \cdot mol^{-1}$) and was found to be independent of both the degree of mechanical activation and the composition of the starting mixture.

1. Introduction

The use of Self-propagating High-temperature Synthesis (SHS) of TiC_{1-x} has been object of numerous studies in the last two decades [1, 2]. SHS reactions can be realized in the composition interval $0.47 \leq \mu \leq 1.9$ (with μ equal to the molar ratio C/Ti), although for $\mu > 1.4$ a pulsed propagation of the reaction front is observed [1]. The lower limit, $\mu = 0.47$, corresponds approximately to the limit of existence of the TiC_{1-x} phase ($Ti_{67}C_{33}$) while the limit $\mu = 1.4$ falls well inside the TiC-Ti binary field [3]. The adiabatic combustion temperature (T_{ad}) for the stoichiometric reaction equals the TiC melting point (3210 K) and decreases for both Ti and C excess [1, 2]. A major effect on the combustion behaviour has been related to the C particle size. The use of fine carbon particles extends the compositional range where SHS occurs and an inverse relationship between wave velocity and C particle size has been observe by several authors. The particle size of Ti has minor or no effect on the reaction kinetics, as Ti is probably completely melted within the reaction zone [2].

Much less attention has been paid to the study of the ignition mechanism, particularly to the evaluation of the dependence of the ignition temperature on materials properties and experimental conditions. The melting of Ti (at 1670°C) is generally considered as a pre-requisite for ignition. Lee and Chung [4] reported that the ignition temperature (T_{ig}) of Ti-C mixtures can be lowered from the range 1650–1700°C (typical of reactions

---

*Author to whom all correspondence should be addressed.

using coarse graphite powders, −325 mesh) to temperatures ranging between 1050 and 1475°C (depending on the reactants stoichiometry) by using carbon black of nominal size below 1 μm.

The aim of the present study is to investigate the role of mechanical activation of the reactant powders by ball milling on the ignition and propagation of combustion reactions in the Ti-C system. Two elemental compositions will be considered, $Ti_{50}C_{50}$ and $Ti_{70}C_{30}$, which approximately correspond to the limiting values for the stability region of TiC.

2. Experimental procedures

Elemental Ti and C powders (99.9% pure) corresponding to $Ti_{50}C_{50}$ and $Ti_{70}C_{30}$ compositions were treated inside a commercial Spex Mixer Mill (model 8000), controlled by a three-phase asynchronous electrical motor at a frequency of 1100 rpm. Milling runs were carried out in continuous mode using powder batches of 6 g and a single milling ball of 11.6 g and 14.2 mm in diameter. Both vial and ball were made of hardened steel. Powder handling and milling were done under an atmosphere of highly purified argon in a glovebox. The impact energy E was equal to 0.164 J corresponding to a milling intensity of 0.75 W/g. Further experimental details are given in a previous publication [5].

Milled powders were then isostatically compacted into cylindrical pellets, 5 mm in diameter and 10 mm in height. The pellets were placed inside a stainless steel reactor and the SHS process was ignited by an electrically heated tungsten coil accurately placed at a distance of exactly 1.0 mm from the top surface of the pellet to ensure reproducibility of the ignition condition. All experiments were conducted in a high purity argon (99.998%) atmosphere. Temperature profiles of the advancing front were recorded by a two-colour single point pyrometer with a resolution time of 0.01 s. Video recordings of the reaction were used to measure the reaction velocity.

The study of the ignition process has been performed acquiring the temperature on the top surface of the reacting pellet with a type S micro-thermocouple (50 μm in diameter). The thermocouples, which had a response time of 10 ms, were connected to an A/D converter with sampling rate of 0.2 kHz. DTA measurements were performed using a TG-DTA Setaram Labsys equipment operated at 30 K/min up to a maximum temperature of 1180°C.

Structural and microstructural characterizations of the mechanically activated powders and combustion products were performed using a scanning electron microscope (SEM, Cambridge Stereoscan 250) and X-ray powder diffraction (Rigaku DMax7B, equipped with a Cu-K_α radiation tube and a graphite monochromator on the diffracted beam).

3. Results

Mixtures in the compositional range $2.33 < \mu < 0.4$ (corresponding to $Ti_{30}C_{70}$ and $Ti_{73}C_{27}$ respectively) undergo Mechanically-induced Self-propagating Reaction (MSR) [5]. Milling time required to initiate MSR (t_{ig}) for given experimental conditions (e.g., impact energy) depends largely on composition, decreasing from $\mu = 2.33$ to $\mu = 0.4$. The occurrence of the MSR is observed in any case before the appearance of any product phase in the milled powders. Samples with the compositions chosen in this present study ($Ti_{50}C_{50}$ and $Ti_{70}C_{30}$) self-ignite after 665 min and 275 min of milling, respectively. SHS experiments have been performed using powder mixtures that were milled for periods that are constant fraction of t_{ig}: 2, 120, 240, 360, 480, and 660 min for the $Ti_{50}C_{50}$ composition and 2, 60, 120, 280, 240, and 270 min for the $Ti_{70}C_{30}$ composition. The effect of milling on both combustion and ignition characteristics of the SHS processes has been investigated. The effect of milling time on reaction temperature and propagation rate is reported in Fig. 1 for the $Ti_{50}C_{50}$ and the $Ti_{70}C_{30}$ compositions. The combustion temperature increases for both compositions, but the increase is more pronounced for the $Ti_{70}C_{30}$ composition. The wave velocity also increases significantly with milling time. In the case of the $Ti_{70}C_{30}$ composition, the velocity increases by a factor of four as the milling time is increased from about 50 min to about 300 min. The velocity change for the equiatomic sample is relatively small initially but increases markedly at longer times. Powders which were milled for about 700 min react with a velocity of about 80 mm · s^{-1}. The apparent activation energy for the combustion was determined using the method proposed by Merzhanov [6]. In this approach the temperature of the combustion process is varied through the addition of various amounts of diluents to the reacting mixture and the relative change in propagation rates and combustion temperatures are determined. On the basis of this approach the propagation rate (v) is related with the combustion temperature and the thermochemical parameters of the reaction products through the relation:

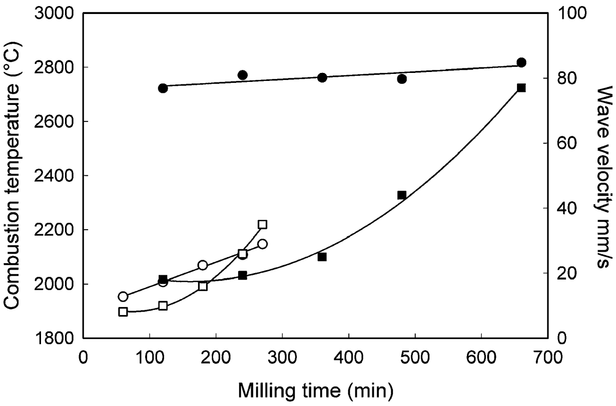

Figure 1 Dependence of the combustion temperature (circles) and wave velocity (squares) on milling time for the compositions $Ti_{50}C_{50}$ (filled symbols) and $Ti_{70}C_{30}$ (hollow symbols).

$$v^2 = f(n)\frac{c_p k}{q}\frac{RT_c^2}{E^*}K_0 \exp\left(-\frac{E^*}{RT_c}\right)$$

where c_p is the specific heat capacity of the products, and k their thermal conductivity, q is the heat of the reaction, T_c is the combustion temperature, $f(n)$ is a function of the kinetic order n of the reaction, K_0

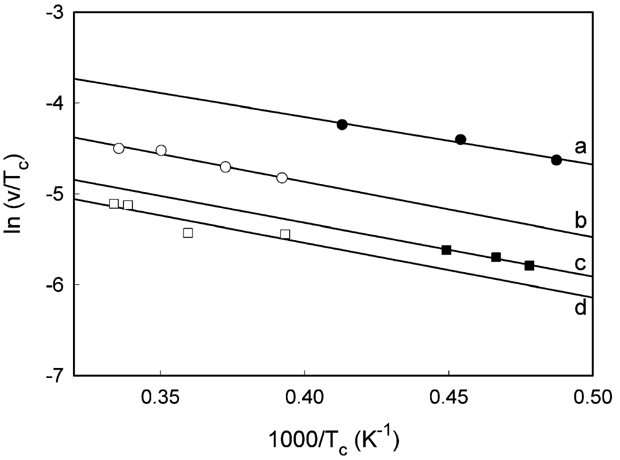

Figure 2 Activation energy plot for the combustion process. a: $Ti_{70}C_{30}$, milling time (m.t.) 270 min; b: $Ti_{50}C_{50}$, m.t. 660 min; c: $Ti_{70}C_{30}$, m.t. 60 min; d: $Ti_{50}C_{50}$, m.t. 120 min.

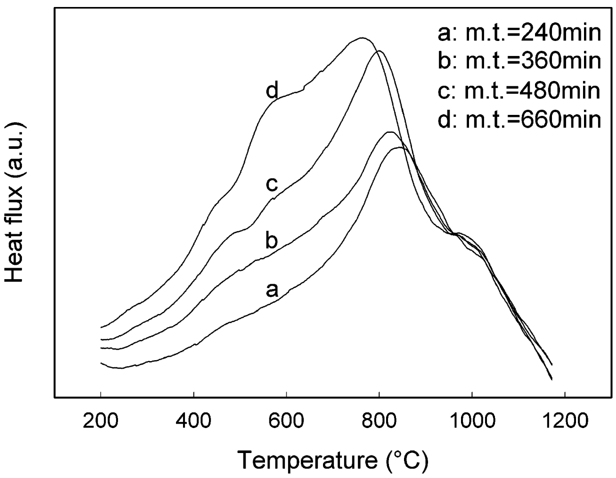

Figure 4 DTA traces recorded at 30 K/min on $Ti_{50}C_{50}$ powder mixtures milled for different times.

is a constant and E^* is the apparent activation energy of the reaction. Thus the slope of $\ln(v/T_c)$ versus $1/T_c$ can provide the apparent activation energy of the process.

In our case the determination of the activation energy was performed on both compositions and for two milling times (120 and 660 min for the $Ti_{50}C_{50}$ composition and 60 and 270 for the $Ti_{70}C_{30}$ composition). The same reaction product (TiC) was used as diluent in amounts varying between 5 and 40 wt% depending on the stoichiometry and milling time. Fig. 2 shows that the milling treatment does not seem to produce any significant change in the slopes of these curves. The calculated activation energy was of 95 ± 5 kJ/mol, which corresponds to the activation energy for the dissolution-precipitation mechanism according to Munir and Anselmi-Tamburini [2]. This result agrees with the mechanism proposed by He and Stangle for the combustion synthesis of niobium carbide [7] which considers the melting of the metal as a process taking place in the zone ahead of the reaction front.

Fig. 3 shows the influence of milling time on the ignition temperature of the two compositions. A pronounced decrease in ignition temperature with an increase in milling time is clearly evident. It should be emphasized that reaction mixtures which had not been milled cannot be ignited. It has been reported that the melting of Ti is necessary in order to observe ignition when graphite powders are used [4]. Since in our experimental setup the maximum temperature that can be achieved on the top surface of the sample is 1400°C, ignition was not possible. Although longer milling time is needed to decrease the ignition temperature of the $Ti_{50}C_{50}$ samples to the same level as that for the $Ti_{70}C_{30}$ samples in both cases the lowest observed ignition temperature is about 500°C. This value is reached in a time close to the MRS event. Fig. 4 shows the results of DTA investigations on the same mixtures used for the ignition experiments. In this case, of course, the heating rate is much lower (30 K/min) of the one experienced by the samples during SHS ignition. The thermograms appear quite complex and indicate a considerable interaction between the reactants at temperatures as low as 500°C. In general one main broad exothermic peak falling around 800°C can be identified. Another, smaller peak at around 600°C is evident (and becomes stronger) at longer milling time. The high temperature peak is relatively insensitive to the milling treatment, while the low temperature "peak" becomes especially evident at long milling times. The peak at around 800°C shows a complex behavior with milling time: it tends to broaden and its maximum value shifts to lower temperatures as milling time is increased.

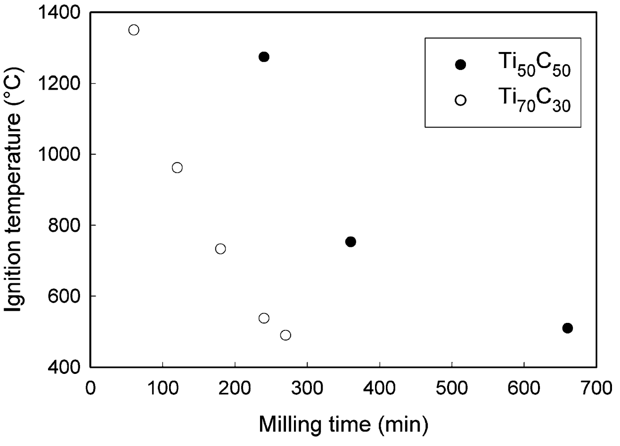

Figure 3 Dependence of the ignition temperature on milling time for the compositions $Ti_{50}C_{50}$ (filled symbols) and $Ti_{70}C_{30}$ (hollow symbols).

4. Discussion

The results of the present study illustrate that milling is an effective method for modifying the characteristics of the SHS processes in the Ti-C system. Most of the results described above can be interpreted on the basis of the evolution of the microstructure of the powder blends during the milling treatment. The milling process produces a microstructure characterized by the presence of large agglomerates of tightly packed reactants. The surface contact area between the reactants is greatly increased, reducing the critical diffusional lengths required for obtaining a significant conversion of the reactants. This produces a faster macroscopic kinetics, leading to a higher rate of heat release and hence to higher temperatures in the combustion front (Fig. 1).

The strong dependence of the wave velocity on milling time is then the result of both increased reaction temperature and the inverse dependence of wave velocity on particle size [8–11]. However, the lack of any significant change in the activation energy for the overall combustion process indicates that the milling process does not change the microscopic reaction mechanism. Once ignited, the reaction invariably involves a liquid phase and thus the rate-limiting step is represented by the diffusion of carbon in the melt, as was confirmed by the value of the activation energy.

Particularly interesting is the large influence that mechanical activation has on the ignition temperature in this system. Modification of the ignition temperature through milling has been invoked to explain occurrence of combustion-like processes during milling [12], but little experimental evidence is available. The heating rates experienced by the sample during the ignition process are much lower than those involved in the propagation of the combustion fronts. As a result, relatively slow processes can play a significant role. Mechanical activation can increase the surface of contact between the reactants up to a level that solid-solid interaction can become the process responsible for ignition. Regular SHS processes, instead, usually require melting of one of the reactants in order to observe ignition, as solid-liquid processes are much faster than solid-solid processes in regular powders. This change in mechanism (to a solid-solid reaction) results in a decrease in the ignition temperature. The extent of this decrease, however, varies considerably for different systems [13]. In this study an unusually large decrease in ignition temperature has been observed for both compositions. Considering that unmilled powders require Ti melting to ignite, a decrease of over 1000°C is observed. The two compositions require different milling times to reach the same ignition temperature (Fig. 3). However, it is evident that ignition temperatures for the two compositions are similar if we consider the same fraction of t_{ig} instead of its absolute value. One possible explanation relies on the fact that the two compositions require different milling times to reach the same level of mechanical activation. Even though it is difficult to define unequivocally a degree of mechanical activation since it is a combination of terms such as particle size, interfacial area, strain, some qualitative indications can be obtained by simply considering the dimensions of the coherent diffraction domains, $\langle L_{hkl} \rangle$. The decrease in the dimension of the coherent diffraction domains is much slower for the $Ti_{50}C_{50}$ composition than for the $Ti_{70}C_{30}$ one, but the interesting point is that a value of $\sim$23 nm was found for both compositions at milling times equal to t_{ig} [5]. Also, as expected, the same dimensions were observed at equal fraction of t_{ig} [5]. However, the DTA results (Fig. 4) indicate that a much more complex situation is likely taking place. The DTA patterns are complex, showing low temperature peaks (already present at quite short milling times) increasing in intensity with an increase in milling time rather than exhibiting a shift of peaks to lower temperatures. The temperature of the first observed thermal effect is also close to the minimum ignition temperature observed in SHS experiments. This suggests that milling produces a mixture of regions with very different microstructures and that the effect of milling is to increase the fraction of the sample with low particle size instead of gradually decreasing the particle size in the entire sample.

5. Conclusions

Reactivity in the Ti-C system was investigated as a function of milling time. Increase of milling time, up to the value at which a combustion-like process ignites spontaneously under milling (t_{ig}), produces a sharp increase in both combustion temperature and wave velocity for both the compositions investigated, $Ti_{50}C_{50}$ and $Ti_{70}C_{30}$.

Milling of the reactants does not change the microscopic reaction mechanism. Once ignited, the reaction invariably involves a liquid phase; the rate-limiting step is represented by the diffusion of carbon in the melt regardless of composition and milling time.

A change of mechanism from a solid-liquid to a solid-solid one was observed on the SHS ignition step. SHS ignition temperature sharply decreases from Ti melting point for unmilled powders to about 500°C for powders milled for a time equal to t_{ig}.

References

1. A. MAKINO, *Progr. Energ. Combust.* **27** (2001) 1.
2. Z. A. MUNIR and U. ANSELMI-TAMBURINI, *Mater. Sci. Rep.* **3** (1989) 277.
3. L. E. TOTH, "Transition Metal Carbides and Nitrides" (Academic Press, New York, 1971).
4. W.-C. LEE and S.-L. CHUNG, *J. Mater. Sci.* **30** (1995) 1487.
5. C. DEIDDA, F. DELOGU, F. MAGLIA, U. ANSELMI-TAMBURINI and G. COCCO, *Mater. Sci. Eng.* A, in press.
6. B. I. KHAIKIN and A. G. MERZHANOV, *Comb. Explos. Shock Waves* **2** (1966) 22.
7. C. HE and G. C. STANGLE, *J. Mater. Sci.* **13** (1998) 146.
8. J. RÄISÄNEN and J. KEINONEN, *Appl. Phys. Lett.* **49** (1986) 773.
9. A. P. ALDUSHIN and B. I. KHAIKIN, *Comb. Explos. Shock Waves* **10** (1973) 273.
10. A. P. HART and P. V. PHUNG, *Comb. Flame* **21** (1973) 77.
11. F. MAGLIA, U. ANSELMI-TAMBURINI, G. COCCO, M. MONAGHEDDU, N. BERTOLINO and Z. A. MUNIR, *J. Mater. Res.* **16** (2001) 1074.
12. G. B. SCHAFFER and P. G. MCCORMICK, *Metall. Trans.* A **22** (1991) 3019.
13. U. ANSELMI-TAMBURINI, F. MAGLIA, S. DOPPIU, M. MONAGHEDDU, G. COCCO and Z. A. MUNIR, *J. Mater. Res.* **19** (2004) 1558.

Received 11 September 2003
and accepted 27 February 2004