Synthesis of Titanium Carbide by Self-Propagating Powder Reactions. 1. Enthalpy of Formation of TiC

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In order to solve the heat equation which describes self-propagating high temperature synthesis (SHS) of refractory materials, a set of experiments have been performed to measure the enthalpy of reaction which accompanies the formation of titanium carbide in direct powder reactions. In air, the measured value is -139 ± 6 kJ·mol^{-1}, whereas in argon it becomes -129 ± 6 kJ·mol^{-1} and can then be assimilated with the enthalpy of formation of TiC. These data are in fair agreement with some previously published results and lead to a calculated adiabatic temperature of 2900 ± 100 K.

Introduction

Once they have been initiated by an external heat source, highly exothermic reactions become self-propagating when the rate of energy generation at the reaction front is larger than the rate of energy loss to the surroundings. The propagation of the reaction is influenced by the thermophysical properties of the materials which form the powder bed (i.e., thermal conductivity, density, and heat capacity), and it also depends on the thermochemical characteristics of the reaction itself, primarily the enthalpy of formation of the product(s) and the energy of activation of the reaction (*1*). It has been suggested (*2*) that the adiabatic temperature must exceed 1800 K in order for a powder reaction to be self-propagating, which sets an empirical, approximate condition on the enthalpy of formation of the product relative to its heat capacity: $\Delta_f H°(298.15\ \text{K})/C_p(298.15\ \text{K}) \geq 2000$ K (*3*). The difference between these two values probably comes from the variation of C_p with temperature. In the case of titanium carbide, the reaction is self-propagating regardless of the degree of compaction of the reactants (*4, 5*). The total conversion of commercial powders of Ti and C, mixed in equimolar amounts, into TiC occurs at a velocity of a few millimeters per second (*4–6*). The final microstructure is porous, and the TiC particles are small (average grain diameter is 2 μm) and surrounded by a grain-boundary phase which is typical of a transient liquid phase (*5*). An X-ray diffraction pattern of the final product shows only the titanium carbide peaks (*7*) without graphite or titanium peaks, only observed in products prepared from nonstoichiometric powders (*8*).

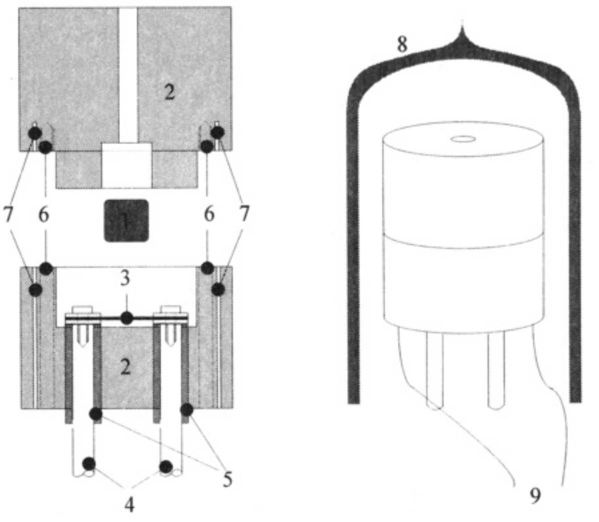
Table 1 lists some published values of $\Delta_f H°$(TiC, 298.15 K) as well as the experimental techniques used (*9–11*). The discrepancy is important, and the present study is aimed at measuring the enthalpy of reaction which accompanies the formation of TiC in direct powder reactions.

Table 1. Previously Published Values of the Enthalpy of Formation of Titanium Carbide

method	$\Delta_f H°$(TiC, 298.15 K)	ref
titanium carbide oxidation studied by high temperature calorimetry; calibration made by known chemical reaction	-183.5 ± 4.0	9
direct reaction from Ti and C powders; high temperature calorimetry in graphite crucible under vacuum; ΔT measured by pyrometry during reaction	-190.4 ± 17.0	10
TiC vaporization; calculation made from titanium vapor pressure measurements	-131.1	11

Experimental Section

The green specimens are prepared from commercial powders of titanium (ref PROLABO 28654.188, lot 306 AP) and graphite (PROLABO 240489.363, lot 306 AP), without further treatment. The raw materials are sifted below 40 μm to ensure easier ignition and propagation, and mixed in equimolar amounts. After dry homogenization in a rotary mill for 24 h, the powder mixture is then compacted inside a silicone mold and cold isostatically pressed at 200 MPa. The samples are cylindrical, about 14 mm in diameter and height, and the relative density is 44%.



(a) (b)

Figure 1. Copper block calorimeter: a, internal details (1, sample; 2, copper block; 3, graphite plate; 4, electrodes; 5, insulating alumina tubes; 6, threaded openings; 7, thermocouple lodging); b, experimental configuration (8, Dewar; 9, E and K thermocouples).

The house-made calorimeter used in this study is illustrated in Figure 1. It consists of two separate cylindrical copper blocks assembled to form a hollow cavity; the calorimeter is set inside a dewar for thermal insulation from the environment, and its total mass is 1.862 kg. The sample inside the cavity is set on a graphite plate electrically heated with copper electrodes to ignite the combustion. The temperature of the copper block is measured with

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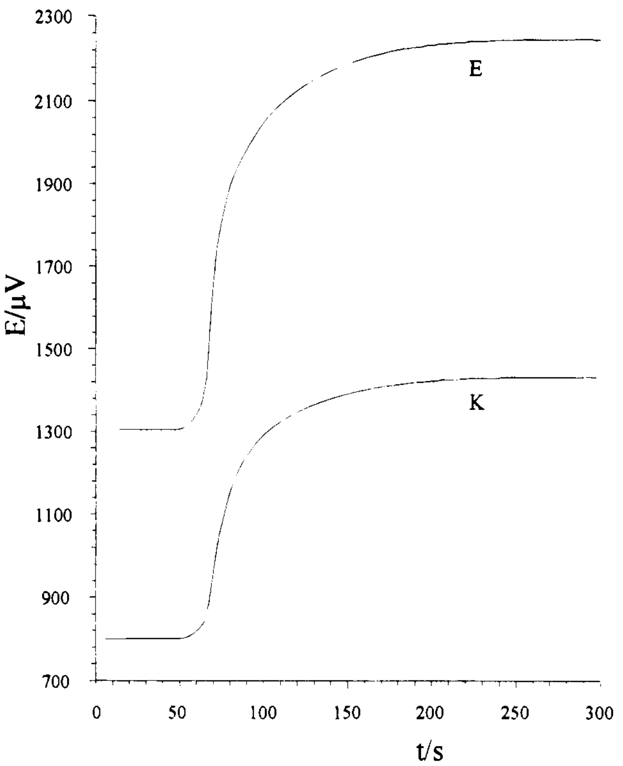

Figure 2. Example of thermocouple output (μV) during an enthalpy measurement made under argon, as a function of time (s) (upper curve, E thermocouple; lower curve, K thermocouple).

Table 2. Experiments Performed in Air[a]

experiment	Q/J	m/g	$\Delta_f H°$(TiC, 298.15 K)/(kJ·mol^{-1})
1	5407.6	2.3145	140.0
2	5730.0	2.3145	148.3
3	6088.0	2.6322	139.4
4	6123.9	2.6322	138.5
5	5586.7	2.3234	144.0
6	3271.7	2.3234	138.5
7	4512.3	1.9974	136.1
8	4297.4	1.9974	129.6

[a] Q is the measured heat for the mass m of the sample. Odd numbers are for measurements by the K thermocouple, even numbers for measurements made by the E thermocouple.

Table 3. Experiments Performed in Argon[a]

experiment	Q/J	m/g	$\Delta_f H°$(TiC, 298.15 K)/(kJ·mol^{-1})
1	3920.5	1.91070	122.9
2	3820.2	1.91070	119.8
3	4558.4	2.02357	134.9
4	4515.4	2.02357	133.7
5	4456.5	2.01054	132.8
6	4393.6	2.01054	130.9

[a] Q is the measured heat for the mass m of the sample. Odd numbers are for measurements made by the K thermocouple, even numbers for measurements made by the E thermocouple.

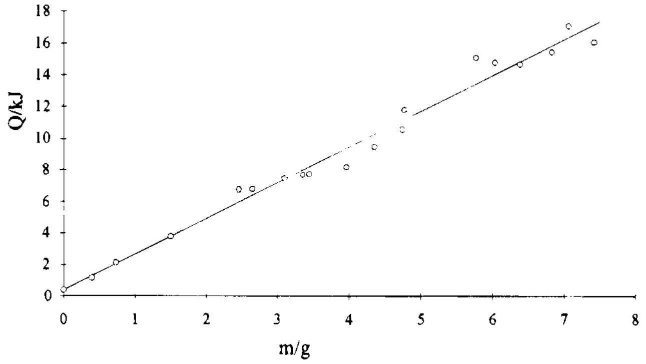

Figure 3. Calorimetry in water: measured enthalpy (kJ) as a function of the mass of the sample (g).

two diametrically opposed thermocouples (one of type E and one of type K), calibrated by bidistillated boiling water, and displaced inside the copper block and connected to a computer. A typical example of temperature recording is shown in Figure 2. As can be seen on this figure, thermal equilibrium in the copper block is reached about 200 s after combustion onset. The temperature rise in the calorimeter is about 10 K; in this temperature interval the heat capacity of copper is considered constant and equal to 385 J·kg^{-1}·K^{-1} (*1*). The cavity is usually filled with air, but experiments have also been conducted in argon after a long out-gassing (30 min) prior to the combustion.

Each combustion experiment is preceded by an experiment without sample aimed at measuring the temperature rise in the copper block due only to the heating of the graphite plate. The combustion which follows is ignited with the same power input in the graphite plate, so that the enthalpy of the combustion itself corresponds to the difference between both ènthalpic effects. This procedure permits the major part of the systematic error due to the calorimeter to be avoided.

Table 2 lists the results of eight measurements made from experiments conducted in air, in terms of measured heats of reaction and the corresponding molar enthalpy of reaction. Table 3 lists the results of similar experiments in argon.

In addition to the aforementioned experiments, the enthalpy of formation of TiC in air has also been measured in a drop calorimeter previously calibrated. This calorimeter is consituted of a known mass of water contained in a dewar in which a sample undergoing combustion is quenched. The temperature rise of the water (up to 15 K) is monitored, and the mass of sample which had reacted is accurately known. Figure 3 reports the results, which show a linear variation of the measured enthalpy of reaction versus the amount of formed TiC. The ordinate at the origin corresponds to the heat received by radiation by the sample from the graphite plate before ignition.

Results and Discussion

The average value measured for the enthalpy of reaction is −139 ± 6 kJ·mol^{-1} for a combustion in air (Table 2), −129 ± 6 kJ·mol^{-1} for a combustion in argon (Table 3), and −135 ± 7 kJ·mol^{-1} for a combustion in air followed by quenching in water (Figure 3). The average mass change which accompanies this reaction is +0.75% in air and −0.38% in argon; these values permit the evaluation of $\Delta_f H°$(TiC, 298.15 K) by taking into account oxidation, vaporization, or both of these effects. The mass gain corresponding to the experiments of Table 2 may be attributed to oxidation, as is indicated by the yellow coloration of the surface of the samples due to the formation of crystalline TiO_2–rutile. In this case, the reaction which has to be accounted for is likely to be

$$\mathrm{Ti_{(s)}} + \mathrm{C_{(s)}} + (3(1-x)/2)\,\mathrm{O_{2(g)}} \rightarrow x\,\mathrm{TiC_{(s)}} + (1-x)\,\mathrm{TiO_{2(s)}} + (1-x)\,\mathrm{CO_{(g)}} + \Delta_r H°(\mathrm{II})$$

where $\Delta_r H°$(II) is the enthalpy of the reaction reported in Table 2 and $x = 0.9775$, issued from mass loss, so that $\Delta_f H°$(TiC, 298.15 K) is calculated as −124 kJ·mol^{-1}. The following values are used in the calculation (*12*): $\Delta_f H°$(TiO_2, rutile) = −944.7 kJ·mol^{-1}; $\Delta_f H°$(CO) = −110.5 kJ·mol^{-1}.

Similarly, the experiments in argon show minor traces of oxidation in spite of the overall mass loss, which may be explained by the occurrence of titanium vaporization due to high temperatures.

The above results suggest that under sufficiently inert conditions the measurements of the enthalpy of formation of TiC are in agreement with the value measured by Fujishiro and Gokcen from equilibrium vapor phase values (-131.1 kJ·mol^{-1} (*11*)), and not too far from the calculated value of -142.3 kJ·mol^{-1} (*13, 14*). As reported by Fujishiro and Gokcen, the discrepancy with the measurements of Humphrey, and of Lowell and Williams, is rather difficult to account for (*11*). Both of those experiments have been carried out at high temperature, with possible cumulative errors concerning heat capacities, as was previously noted by Lowell and Williams (*10*). In addition, these researchers worked in a graphite crucible, which is not inert under the conditions of the reaction, and measured the temperature elevation by pyrometry. On the contrary, the method we have chosen only needs the heat capacity of copper, near the ambient temperature in a small temperature range ($\Delta T = 15$ K).

When combustion is conducted in air, the amount of heat evolved in the reaction is -139.3 ± 5.5 kJ·mol^{-1}, due to surface oxidation. This latter value leads to an adiabatic temperature $T_{\mathrm{ad}} = 2900 \pm 100$ K calculated by the relationship

$$\Delta_f H^\circ(\mathrm{TiC},\ 298.15\ \mathrm{K}) + \int_{T_0}^{T_{\mathrm{ad}}} C_p(\mathrm{TiC})\,\mathrm{d}T = 0$$

using C_p(TiC) found in ref 15. Despite a similar accuracy, the experiments carried out in argon are more reliable, as the effect of oxidation is less important. The measurements performed in water have led to an enthalpy of formation intermediate between those obtained under inert and oxidized conditions. The difference in the energy measured by the copper block and by water calorimetry can be attributed to the radiative heat loss before the sample is quenched; under the present experimental conditions, it amounted to 4 kJ·mol^{-1}.

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