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Real-Time Measurement on the Heat Release Property of Titanium Blended with Different Carbon Allotropes, under Externally Constant Heat Flux

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Abstract: Ti/C blended powder is commonly employed as an initiating combustion agent for preparing calcium aluminate; a dedicated test system is exploited for real-time examining of the heat release of Ti/C blended powder during combustion under atmosphere conditions with an externally constant heat flux of 973 K, which is comprised of cone calorimeter, thermal-gravimetry/differential scanning calorimetry, X-ray diffraction (XRD), scanning electron microscope/energy dispersive spectrometer, and a theoretical thermal calculation, with the aim of quantitatively illuminating its combustion mechanism in depth. Furthermore, a comparison of the heat release property of titanium powder blended with different carbon allotropes, including natural flaky graphite (FG), carbon black (CB), expandable graphite (EG), and vermicular graphite (VG) is preliminarily investigated, to clarify the effect of different carbon allotropes on the heat release property of Ti/C blended powder. It reveals that the oxidation reaction between Ti and O₂ initiates the subsequent combination of TiC through a thermal explosion reaction, using graphite (FG, VG, or EG) and Ti powder as the starting materials, respectively. Moreover, EG facilitates an accelerated (fire growth index of 0.42 kW·m⁻²·s⁻¹) and enhanced peak heat release rate (pHRR) of 30.7 kW·m⁻² at 73 s, while VG suppresses the heat release with the pHRR of 5.2 kW·m⁻² at 64 s and fire growth index of 0.08 kW·m⁻²·s⁻¹, and FG favors the formation of TiC with a higher crystallinity from XRD. Additively, the prior NaOH-impregnation is favorable for the formation of TiC for Ti/CB blended powder, although the TiO₂ predominates final combustion production. It reveals the chemical evolution and mechanisms evolved in the formation of TiC during ignition.

Keywords: titanium carbide; heat release properties; graphite; thermodynamic calculation; cone calorimeter; TG/DSC

1. Introduction

Titanium carbide (TiC) is a good reinforcement for titanium matrix composites via self-propagating high-temperature synthesis (SHS), with many manifest advantages [1,2], due to its chemical compatibility with Ti, high hardness and Young's modulus, and high flexural strength [3], which is commercially produced by the overall reaction of TiO₂(s) + C(s) = TiC(s) + 2CO(g) under 1973–2373 K, using Ti powder and carbon black as the starting materials typically [4]. Simultaneously, the Ti/C blended powder is commonly employed as the initiating combustion agent for preparing calcium aluminate via SHS [5,6]. Nevertheless, there is little literature on real-time testing of the heat release property during combustion of Ti/C blended powders, leading to the unclear chemical evolution and mechanisms evolved in reaction and growth of TiC both prior to, during, and after ignition [7].

In addition, the graphite or amorphous carbon black (CB) is mainly exploited as the carbon source for preparing TiC under an inert atmosphere [4,7–10]. The general consensus is that graphite

contains expandable graphite (EG), vermicular graphite (VG), or expanded graphite after instantaneous expansion of EG, and natural flaky graphite (FG), which hold obviously different micro-structures and properties. Therefore, the various carbon sources affect the productions formed by SHS reaction [11]. It has been reported that the carbon nanotube and graphene as carbon sources impart enhanced tribological properties [12]; CB favors the formation of nano-metric TiC-carbon composite with a smaller particle size, as the most effective carbon allotrope for hindering the sintering of TiC under high temperature [13]. However, there is an interesting phenomenon—that the explosive reaction between graphite and titanium powder occurs under atmospheric pressure at 973 K with a transiently glaring flame, which inspired us to excavate its reaction mechanism, in order to explain the curious phenomenon.

Consequently, the real-time measurement of heat release property involved in titanium blended with different carbon allotropes is preliminarily investigated, which is detected and recorded by cone calorimeter (CC) and thermal-gravimetry/differential scanning calorimetry (TG/DSC), respectively, using FG, CB, EG, and VG as different carbon sources to react with titanium powder at an external heat flux of 973 K. Meanwhile, the mercerization of different carbon allotropes by NaOH-impregnation aims to investigate the effect of impurities involved in various carbon sources on the explosive reaction of Ti/C blended powders, due to that the impurities mainly belong to combustible organics within CB, which are prone to transform into volatiles and disturb the solid-state reaction involved in Ti/C blended powders. Furthermore, the microstructure of reaction product is examined by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. It aims to seek an effective avenue to deepen the reaction mechanism involved in the combustion of Ti/C blended powders. The novelty of this article is exploring an effectively quantitative method to clarify the mechanism of the period both prior to, and during combustion of Ti/C powder, using Ti and different carbon allotropes as the starting materials.

2. Materials and Methods

2.1. Raw Materials

The grey titanium powder was purchased from Tianjiu chemical group of Changsha in China, with an average particle size of 85 μm . Carbon allotropes, including EG with an average particle size of 320 μm and a volume expansibility 400 $\text{mL}\cdot\text{g}^{-1}$, CB, VG, or FG with an average particle size of 85 μm , were all fabricated by Qingdao Tengsheng chemical group.

The XRD patterns of raw materials are presented in Figure 1; the hexagonal titanium (Ti, JCPDS 44-1294) is clearly detected. The graphite (C, JCPDS 41-1487) predominates the carbon allotropes, including FG, EG, and VG, but CB mainly consisted of the amorphous carbon (corresponding to the hump of 2θ at 15° – 30°).

The following samples denoted as S1–S9 were our research objectives: The S1 was neat Ti powder. The S2 was comprised of Ti and FG, S3 consisted of Ti and CB, S4 consisted of Ti and EG, and S5 consisted of Ti and VG. Additively, S6–S9 were the samples comprised of Ti and NaOH-impregnated carbon allotropes corresponding to S2–S5. And the NaOH-impregnation was conducted by dispersing the carbon powder (10 g) into the 8 mol L^{-1} NaOH (200 mL) for 24 h under isolated air at room temperature; then the filter residue obtained by suction filtration was deionized water-washed to neutrality ($\text{pH} = 7$); the final mercerized carbon allotropes were collected through vacuum drying at 333 K. The FG–NaOH represented the FG subjected to NaOH-impregnation, the EG–NaOH, CB–NaOH, and VG–NaOH were assigned to the EG, CB, and VG after mercerization of NaOH, respectively. The atomic molar ratio of Ti/C mixture equaled 1 in S2–S9 corresponding to a Ti/C weight rate of 4:1. The sample was subjected to a mechanically ball-grinding blending (15 min with a rotational speed of 100 rpm at room temperature) before reaction in CC.

Figure 1. XRD of raw materials including titanium, flaky graphite (FG), carbon black (CB), expandable graphite (EG), and vermicular graphite (VG).

2.2. Characterizations

The real-time heat release rate (HRR) was examined by ZY6243 CC (Zhongnuo instrument company, Dongguan, China). The 12 g sample located on aluminum foil was placed horizontally to an external heat flux of $40 \text{ kW} \cdot \text{m}^{-2}$ (973 K approximately) for reactions with a vertical interval of 25 mm. Simultaneously, the time to ignite (TTI), the peak heat release rate (pHRR), and the time to pHRR (t_p) were automatic recorded. Total heat release (THR) was the cumulative heat release during the whole reaction except the external heat flux. The fire performance index (FPI) was defined as the ratio of TTI to pHRR ($\text{FPI} = \text{TTI}/\text{pHRR}$), and the fire growth index (FGI) was defined as the ratio of pHRR to t_p ($\text{FGI} = \text{pHRR}/t_p$) [14,15], which were important parameters to evaluate the heat release property.

A Mettler analyzer (Germany) was exploited to accomplish the TG/DSC analysis under the simulated atmosphere condition during the heating from 323 to 1273 K with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. Microstructures of samples after reaction were characterized by Quanta 200 SEM, and D/MAX-2400 X-ray diffractometer with Cu K α radiation, respectively.

3. Results

3.1. HRR of Ti Blended with Different Carbon Allotropes

The S5 comprised of VG and Ti presents the lowest pHRR value of $5.2 \text{ kW} \cdot \text{m}^{-2}$ among all Ti/C blended samples during the whole reaction, as shown in Figure 2a, due to the worm-like structure of VG, which traps and suppresses the transfer of heat and mass. S4, comprised of EG and Ti, exhibits the highest value ($30.7 \text{ kW} \cdot \text{m}^{-2}$) of pHRR at 73 s, due to the vigorous expansion of EG, which accelerates the propagation of combustion wave, prompting the heat and mass transfer.

Figure 2. Heat release rate (HRR) of samples recorded by cone calorimeter (CC), including Ti/C blended powder before (a) and after (b) NaOH impregnation of carbon allotropes.

The CB, owing to its high-activity and amorphousness, is prone to form a carbonaceous barrier to inhibit and dilute the heat under non-equilibrium, leading to the obviously retarding and shrunken peak with the pHRR value of $12.5 \text{ kW}\cdot\text{m}^{-2}$ at 152 s. Furthermore, there is a sharp exothermic apex at 422 s corresponding to the combustion of raw CB, as shown in Figure 2a, while no peak is detected for the raw FG, indicating that pristine CB holds obvious and testable combustibility.

After NaOH-impregnation of carbon allotropes, the shrunken and lower HRR curves are clearly examined for S7 and S8 compared with those of S3 and S4, as shown in Figure 2b, due to the impurities eliminated by NaOH, leading to a remarkable increase in FGI, which rose from 0.08 to $0.12 \text{ kW}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ for S3 (Table 1). However, the S6 exhibits a retarded T_p with a decreased FGI compared with that of S2, due to the stable and inert structure of FG under the strong alkali-condition; it could have served as a heat dissipation filler, due to its high thermal conductivity [16].

Nevertheless, the increased pHRR and FGI are detected for S9 compared with that of S5, due to the subdued trapping effect of impurities after NaOH-impregnation, leading to an earlier T_p . It is worth pointing that the T_p of sample with EG or VG emerges at nearly the same time, because the prior heating

makes the EG rapidly expand and transform into VG with worm-like structure at beginning of reaction. That is the same reactants present a similar reaction pathway except for the rapid expansion of EG.

Table 1. HRR properties of samples tested by CC.

Samples	Ingredient	TTI/s	THR/kW	pHRR/kW·m ⁻²	T _p /s	FPI/s·m ² ·kW ⁻¹	FGI/kW·m ⁻² ·s ⁻¹
S1	Pure Ti	3	2.51	9.6	71.2	0.31	0.13
S2	Ti + LP	16	8.77	14.9	85.5	1.07	0.17
S3	Ti + CB	25	8.46	12.5	151.6	2.00	0.08
S4	Ti + EG	2	17.19	30.7	72.9	0.07	0.42
S5	Ti + VG	30	6.08	5.2	64.3	5.77	0.08
S6	Ti + LP-NaOH	28	8.11	16.4	110.1	1.71	0.15
S7	Ti + CB-NaOH	16	5.43	8.5	71.2	1.88	0.12
S8	Ti + EG-NaOH	2	7.01	23.8	44.5	0.08	0.53
S9	Ti + VG-NaOH	35	2.78	7.9	45.1	4.43	0.18

Table 1 lists the heat-releasing parameters of samples, the S4 comprised of EG and Ti exhibits the highest FGI value of 0.42 kW·m⁻²·s⁻¹, while the S3 presents the lowest FGI of 0.08 kW·m⁻²·s⁻¹ (the same to that of S5), implying that the CB or VG inhibits the flame propagation effectively [14,15]. Because the EG transforms into fluffy worm-like structure with a vigorous expansion, it facilitates the propagation of combustion wave and heat transfer further due to the loose and fluffy stacking, which favors an extremely vigorous and energetic process [17], evidenced by the decrease in TTI and the rapid increase in HRR. However, the mercerization of NaOH favors the purification of carbon allotropes; the impurities could have transformed combustible volatiles and produced a higher heat release, evidenced by the decrease in the THR for samples with carbons after NaOH-impregnation. Meanwhile, they also transformed into char residues under the intensely heat-releasing condition, together with the traces of silicates, phosphates, and sulfates involved in EG or VG, which blocked or disturbed the solid-state reaction between activated Ti and carbon, leading to an obvious decrease in the THR. Because the sharp temperature-rising facilitates the formation of shielding char, it prevented further cracking of the pyrolysis products into non-condensable compounds [18].

3.2. XRD of Samples after Reactions in CC

The minerals contain khamrabaevite (TiC, JCPDS 32–1383, K) [19], tetragonal rutile (TiO₂, JCPDS 21–1276, R), orthorhombic titanium oxide (TiO₂, JCPDS 21–1236, T), and graphite (C, JCPDS 41–1487, G) are detected as shown in Figure 3. Pure Ti mainly transforms into titanium oxide and rutile. However, the coexistence of predominant TiC and a slight TiO₂ was confirmed for samples with FG, EG or VG, revealing that the formation of TiC is feasible under atmospheric conditions at 973 K, and the sharper and narrower peaks are attributed to the TiC with a higher crystallinity [20]. Meanwhile, a small quantity of rutile is formed and some graphite left, which clearly determines that the off-stoichiometric reaction occurs between Ti and graphite, due to the non-equilibrium condition and the dominated slow solid-state reaction. On the contrary, the sample S3 comprised of CB and Ti mainly presents the peaks corresponding to TiO₂ and rutile; the hump of 2θ at 25°–28° assigned to amorphous graphite was recorded, and implies that complicated reactions occur, which will be discussed later.

Additively, some interesting phenomena are observed in the patterns of XRD after the NaOH-impregnation of carbon allotropes, as shown in Figure 4. The sharper peaks corresponding to TiC with a higher crystallinity are detected for S6 and S8 respectively, compared with those of S2 and S4 in Figure 4a,b, which indicates that the NaOH-impregnation favors the formation of TiC through the direct solid-state reaction between Ti and C at 973 K.

The NaOH could eliminate the impurities involved in various carbon sources, which hinder or disturb the solid-state reaction. Meanwhile, the shrunk peaks corresponding to graphite are observed in the pattern of S7; the sharper peaks corresponding to TiO₂ and the small peaks corresponding to TiC emerge in Figure 4c. When compared with those of S3, they reveal that the pre-treatment of CB by NaOH-impregnation affects the reactions significantly.

Figure 3. XRD of Ti/C samples after reactions in CC. K—khamrabaevite, R—rutile, T—titanium oxide, and G—graphite.

Figure 4. *Cont.*

Figure 4. Comparative patterns of Ti/C blended powder before and after NaOH impregnation of carbon allotropes including (a) Ti/FG, (b) Ti/CB, and (c) Ti/EG. K—khamrabaevite, R—rutile, T—titanium oxide, and G—graphite.

Generally, the solid-state reaction of TiC-forming occurs, and the prior NaOH-impregnation of carbon allotropes promote and strengthen the reaction. Moreover, it is suspected that the reactions involved in Ti/C blended powder mainly contain the following Equations (1)–(8), and the thermodynamic data including enthalpy ΔH and Gibbs free energy ΔG is briefed in Table 2, which is clarified later.

Table 2. Thermodynamic data of reactions.

T/K	Equation (1)/kJ $\times$ mol ⁻¹		Equation (2)/kJ $\times$ mol ⁻¹		Equation (3)/kJ $\times$ mol ⁻¹		Equation (4)/kJ $\times$ mol ⁻¹	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
273	-1154.3	-1107.7	-184.6	-181.2	551.5	500.0	366.9	318.8
373	-1154.3	-1090.7	-184.4	-180.0	551.2	481.2	366.8	301.1
473	-1153.9	-1073.7	-184.1	-178.9	550.4	462.5	366.3	283.6
573	-1153.4	-1056.8	-183.8	-177.8	549.4	444.0	365.5	266.2
673	-1152.8	-1039.9	-183.7	-176.8	548.2	425.7	364.6	248.9
773	-1152.1	-1023.2	-183.7	-175.8	547.1	407.6	363.5	231.8
873	-1151.3	-1006.6	-183.8	-174.7	546.1	389.6	362.3	214.9
973	-1150.6	-990.1	-183.9	-173.7	545.0	371.8	361.1	198.1
1073	-1149.8	-973.6	-184.3	-172.6	544.2	354.0	359.9	181.4
1173	-1148.9	-957.3	-189.4	-171.4	548.0	336.2	358.6	164.8
1273	-1148.1	-941.0	-189.2	-169.9	546.6	318.3	357.4	148.3

T/K	Equation (5)/kJ $\times$ mol ⁻¹		Equation (6)/kJ $\times$ mol ⁻¹		Equation (7)/kJ $\times$ mol ⁻¹		Equation (8)/kJ $\times$ mol ⁻¹	
	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG
273	539.1	443.2	-364.3	-329.0	-1154.3	-1107.7	-871.4	-848.3
373	540.0	407.9	-364.4	-316.0	-1154.3	-1090.7	-870.8	-839.9
473	539.9	372.5	-364.1	-303.1	-1153.9	-1073.7	-870.2	-831.7
573	539.1	337.2	-363.5	-290.2	-1153.4	-1056.8	-869.6	-823.6
673	537.8	302.1	-363.0	-277.5	-1152.8	-1039.9	-869.1	-815.6
773	536.1	267.2	-362.4	-264.8	-1152.1	-1023.2	-868.6	-807.7
873	534.1	232.5	-361.8	-252.2	-1151.3	-1006.6	-868.2	-799.9
973	532.0	198.1	-361.3	-239.7	-1150.6	-990.1	-867.7	-792.1
1073	529.8	163.8	-361.0	-227.3	-1149.8	-973.6	-867.3	-784.3
1173	527.6	129.8	-365.2	-214.7	-1148.9	-957.3	-866.9	-776.6
1273	525.2	96.0	-364.3	-201.9	-1148.1	-941.0	-866.5	-769.0

3.3. TG/DSC of Samples

Figure 5a presents a single peak in DTG corresponding to the formation of TiO₂ according to the result of XRD, leading to an exothermic peak at 1047 K with a heat release of 19.1 kJ·g⁻¹ and a sharp weight increase of 164%, and the theoretical enthalpy and weight increments are about 19.5 kJ·g⁻¹ and 167% for the Ti completely transforms into TiO₂ as Equation (1), which indirectly reveal that there is some unreacted Ti, evidenced by the pattern of XRD. And the temperature corresponding to DTG_{max} is 1053 K with an initial weight increase temperature of 950 K, which is mainly assigned to the formation of TiO₂.

Figure 5. Cont.

Figure 5. Cont.

Figure 5. Thermal-gravimetry/differential scanning calorimetry (TG/DSC) of samples, including (a) S1, (b) S2, (c) S3, and (d) S4.

According to the theoretically chemical calculation for the Ti/C blended powder, the theoretical enthalpies for Equations (2) and (6) are $15.6 \text{ kJ}\cdot\text{g}^{-1}$ and $6.0 \text{ kJ}\cdot\text{g}^{-1}$, and the weight increases are 35% and 22%, respectively. It is worth pointing that the S2 and S4 exhibit the same final weight of 133%, as shown in Figure 5b,d, indicating that the formation of TiC occurs predominantly. Nevertheless, S3 presents first, a weight loss, and subsequently, a weight increase with a final weight of 159%, taking on two exothermic peaks at 907 K and 1065 K in Figure 5c. The former is attributed to the oxidization of combustible hydrogen, carbon, and other impurities within CB [21], leading to a continuous weight loss with a peak valley at 930 K. The latter is mainly attributed to the formation of TiO_2 , leading to a rapid weight increase combining with the results of XRD.

However, a slight weight loss at 520 K corresponding to the expansion of EG is recorded for S4, and the exothermic peak ($13.2 \text{ kJ}\cdot\text{g}^{-1}$) at 1040 K is weaker than others in Figure 4d, due to the endothermic transformation from EG to VG. Two obvious DTG_{max} at 946 and 1121 K are observed, with an initial weight increase temperature of 1014 K, implying a retarding effect involved in the formation of TiO_2 and TiC, ascribed to barrier effect of worm-like graphite [13].

3.4. Morphologies of Samples after Reaction in CC

3.4.1. Macro-Appearances of Samples after Reactions

The pure Ti is mainly transformed into a yellow-white solid, as shown in Figure 6a, corresponding to the TiO_2 . As for the S2 comprised of FG and Ti, the non-uniform morphology identifies an incomplete reaction in Figure 6b. When the CB is used as the starting material, a higher content of yellow-white solid is observed in Figure 6c. Additively, the fluffy worm-like graphite covers the underlying solid in Figure 6d, implying that a vigorous expansion occurs during the reaction. But the brownish black powder (similar to the mixture without reaction) is observed in Figure 6e, due to the under-reacting combination.

S6, S7, and S8 (Figure 7a–c) exhibit similar appearances in comparison to that of S2–S4, but S9 takes on an obviously different appearance compared with that of S5. The yellow and black solids (in Figure 7d) reveal that the NaOH-impregnation plays a crucial role in the reaction of Ti/VG powders, compared with the brownish black appearance for S5.

Figure 6. Macro-appearances of samples without NaOH impregnation after reactions in CC, including (a) S1, (b) S2, (c) S3, (d) S4, and (e) S5.

Figure 7. Macro-appearances of samples subjected to NaOH-impregnation after reactions in CC including (a) S6, (b) S7, (c) S8 and (d) S9.

3.4.2. Micro-Morphologies of Samples after Reaction

The irregular pillared-rutile is observed in Figure 8a, and the amorphous TiC covered on the underlying matrix is observed in Figure 8b, which consists of polyhedral grains intimately fused with clean grain boundaries [22,23]. However, the lower regularity of rutile is observed than that of S1, and lots of amorphous graphite particles are dispersed in the clearances of TiO_2 in Figure 8c, due to the insufficient time derived from the non-equilibrium condition and barrier effect of CB [24]. The porous and fluffy worm-like graphite mixed with the TiC appears in Figure 8d, and more dissociated and rugged fracture surface is observed in Figure 8e, due to the retarding effect of worm-like structures. Generally, the formation of TiC is examined and verified, but the high retained porosity is observed owing to its inherent limitation of combustion synthesis [25].

After NaOH-impregnation of carbon allotropes, the continuous and uniform fracture surface is observed in Figure 9, because the mercerization is beneficial to remove the impurities and make the inert char residues decrease, which indirectly accelerates the solid-state reaction between Ti and C, as well as the reaction between Ti and O_2 , leading to the appearance of TiC with a higher crystallinity in Figure 9a. The unreacted graphite is absent in Figure 9b in comparison to that in Figure 8c, and the TiO_2 is mainly the reaction production. Furthermore, the smooth and uniform appearances in Figure 9c are assigned to the fluffy graphite lamellar; the TiC disperses or inserts into the interstitial lamellar. While the bigger particles emerge for S9 (in Figure 9d) than that of S5 (in Figure 8e), due to the enhanced solid-state reaction including formations of TiC and TiO_2 .

Figure 8. SEM of samples after reactions in CC (10,000 × magnification), including (a) S1, (b) S2, (c) S3, (d) S4, and (e) S5.

Figure 9. SEM of samples subjected to NaOH-impregnation after reactions in CC (10,000 × magnification), including (a) S6, (b) S7, (c) S8 and (d) S9.

4. Discussion

The discrepancy between the results of CC and DSC was discovered, obviously. S3 comprised of Ti and CB exhibits the lowest pHRR value and the highest value of heat release tested by DSC, while the S4 comprised of Ti and EG exhibits the highest value of pHRR and the lowest heat release tested by DSC. Because the radiation cone in CC was heated to 973 K prior to measurement, the EG expanded quickly and transformed into fluffy and loose-stacked powder from the beginning of reaction; together with the non-equilibrium condition derived from the extremely rapid heat release, they provide the suddenly increased pathways for the diffusion of O_2 , and accelerate the combination of Ti, O_2 , and graphite, leading to the enhancement of HRR. Nevertheless, the slow-heating DSC provides a uniform and sufficiently equilibrated condition for the reaction, leading to a step-by-step reaction and a complete combination. The combustible materials in CB carbonizes and transforms into non-combustible char residues, which inhibits the flame propagation and dilutes the reactants, leading to a sharply reduced HRR, evidenced by the two obvious exothermic peaks in DSC curve. Zhu et al. [26] also found that delaying flammability caused a reduced HRR with an enhanced heat release.

On the other hand, the prior oxidation of Ti releases the heat (reaching 2513 K) under atmospheric conditions [27], which promotes the thermal explosion reaction between the Ti and C powders due to the chemical oven mechanism, leading to the formation of TiC. According to the literature [28,29], the dissolution-precipitation mechanism mainly governs the formation of TiC, whereas the diffusion of carbon to the Ti molten liquid is the prerequisite. But the insufficient time limits the completion of the dissolution and diffusion processes; the intensely releasing heat disturbs the formation of a continuous carbide layer around the Ti particle during the thermal explosion reaction [29]

However, TiC could also be synthesized by mechanical milling [30], or by rapid combustion-type behavior at 873 K [31]. Consequently, the reaction-diffusion mechanism involved in the formation of TiC at atmosphere condition with an externally constant heat flux of 973 K could be elaborated as the following processes, combining with the thermodynamic calculation. The pure Ti mainly reacts with the O₂ derived from air, as in Equation (1), and transforms into rutile and TiO₂ with a sharp increase in the weight, but the coexistence of TiO₂ and Ti was detected due to the non-equilibrium condition derived from the extremely rapid heat release. Meanwhile, the diffusion of carbon towards the surfaces of TiO₂ and Ti occurs, which provides the formation condition for TiC, together with the intensively releasing heat, led to the explosive reactions with a transiently glaring flame. Additively, the expansion of EG favors the surface reactions between O₂ and Ti [32]. The formation of TiO₂ (Equation (1)) is easier than that of TiC (Equation (2)), evidenced by the higher enthalpy in Table 2, and the formation of TiO₂ releases a higher heat amount for subsequent combination of TiC, leading to the obviously enhanced characteristic peaks corresponding to TiC. Besides, the subsequent reduction reaction between CO (derived from the transformation of impurities in CB) and Ti left preferentially occurs, as in Equation (6), due to the higher Gibbs enthalpy (Equations (3)–(5)) not occurring (due to their positive ΔG s), which is completely consistent with the literature [33,34]. But the oxidation of TiC takes place as Equation (8), due to the higher ΔH and ΔG than that of Equation (7) above 973 K, leading to the absence of TiC for S3. However, the NaOH-impregnation causes the appearance of TiC, which might be contributed to the low THR of S7 (5.43 kW compared with 8.46 kW of S3) limiting the oxidation of Equation (8), leading to slight TiC content remaining.

The solid-state reaction between FG and Ti is beneficial towards forming the TiC, but the quantitative research and mechanical performance of the synthesized TiC need to be studied further, and the modification on its micro-structure holds great potential in our future research, including the interface characteristics among the TiC, rutile, and graphite.

5. Conclusions

Ti/C blended powder is commonly employed as initiating combustion agent for preparing novel calcium aluminate cement, but the heat release of Ti/C blended powder during the whole reaction has not been explored yet. Therefore, an effective and comprehensive test system was used to real-time examine the heat release of reaction within Ti/C blended powder under atmospheric conditions, with an externally constant heat flux of 973 K, containing the techniques CC, TG/DSC, XRD, and SEM, providing necessary data to deepen the reaction mechanism. To quantitatively illuminate its combustion mechanism further, a comparison on the heat release of titanium with different carbon allotropes (FG, EG, VG, and CB) was preliminarily investigated. The rapid expansion of EG accelerates the O₂ diffusion and heat-transfer, and intensifies the non-equilibrium condition, leading to the accelerated and enhanced pHRR of 30.7 kW·m⁻² at 73 s. However, the CB enriched amorphous impurities mainly transforms into TiO₂, which traps the volatiles and retards the transfer of heat/mass effectively, leading to an obvious barrier effect under the non-equilibrium condition, evidenced by the pHRR of 12.5 kW·m⁻² at 152 s. FG and VG favors the formation of TiC with a higher crystallinity, and the prior NaOH-impregnation plays a negligible role in the combination of TiC for Ti/FG blended powder, apart from the formation of TiC with a higher crystallinity, as well as for the Ti/EG and Ti/VG blended powders. Additively, the NaOH-impregnation is favorable for the formation of TiC for Ti/CB blended powder. The theoretically thermal calculations demonstrate that the heat release derived from the oxidation reaction between Ti and O₂ initiates the combination of TiC through thermal explosion reaction, and the subsequent oxidation reaction between TiC and O₂ also occurs slightly.

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