J. Am. Ceram. Soc., **96** [3] 950–956 (2013)
DOI: 10.1111/jace.12079

Journal

Reaction Pathway of Combustion Synthesis of Ti_5Si_3 in Cu–Ti–Si System

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The reaction pathway of combustion synthesis (CS) of Ti_5Si_3 in Cu–Ti–Si system was explored through a delicate microstructure and phase analysis on the resultant products during differential thermal analysis (DTA). The formation of Cu–Si eutectic liquids plays a key role in the reaction pathway, which provides easy route for reactant transfer and accelerates the occurrence of complete reaction. Cu initially reacted with Si to form Cu_3Si by a solid-state diffusion reaction, which further reacted with Cu to form Cu–Si liquids at the eutectic point of ~802°C; then Ti was dissolved into the surrounding Cu–Si liquids and led to the formation of Cu–Ti–Si ternary liquids; finally, Ti_5Si_3 was precipitated out of the saturated liquids by a solution–reaction–precipitation mechanism. The reaction pathway in CS of titanium silicide (Ti_5Si_3) could be described briefly as: $Cu_{(s)} + Ti_{(s)} + Si_{(s)} \rightarrow Cu_3Si_{(s)} + Ti_{(s)} + Si_{(s)} \rightarrow (Cu\text{–}Si)_{(l)} + Ti_{(s)} \rightarrow (Cu\text{–}Ti\text{–}Si)_{(l)} \rightarrow Cu_{(l)} + Ti_5Si_{3(s)}$.

I. Introduction

The synthesis of structural intermetallic compounds in conventional methods is based on the classical processes of powder metallurgy (PM), hot isostatic pressed and reaction hot pressed as well as arc melting,[1–3] all of which share the common feature of using strong external heating to accelerate processing. Compared with such conventional techniques, however, combustion synthesis (CS), also termed as self-propagating high-temperature synthesis, has attracted more attention due to its advantages of lower energy consumption, higher time efficiency and higher product purity, which is preferred in preparing various refractory materials, such as TiC, Al_2O_3, ZrB_2, Ti_3SiC_2, $MoSi_2$, Nb_5Si_3, and Ti_5Si_3, etc.[1,3–8] Recently, titanium silicide (Ti_5Si_3) has attracted considerable attention due to its outstanding properties including high melting temperature (2130°C), low density (4.32 g/cm^3) and high hardness, as well as excellent strength at elevated temperature and high oxidation resistance,[9–14] which consequently promote Ti_5Si_3 as a promising material for high–temperature structural applications.[9–18]

To effectively control the CS process and eventually to obtain desired reaction products, the reaction pathway of Ti–Si system to form Ti_5Si_3 was investigated intensively. Trambukis and Munir[19] proposed that the combustion reaction of Ti and Si proceeded via a series of intermediate interactions in accordance with Ti–Si equilibrium phase relations, i.e., $TiSi_2 \rightarrow TiSi \rightarrow Ti_5Si_4 \rightarrow Ti_5Si_3$. Moreover, Riley *et al.*[20,21] reported that the CS of Ti_5Si_3 was triggered by the phase transformation of α–Ti→β–Ti and followed by a direct solid-state reaction of β–Ti and Si. In addition, Yeh *et al.*[22] suggested that the formation mechanism of Ti_5Si_3 was dominated by the solid–liquid interactions involving the dissolution of solid reactants into the liquid and the precipitation of the final product.

An alloying addition to Ti–Si system was reportedly a possible way to improve the microstructures and mechanical properties (e.g., fracture toughness) of Ti_5Si_3.[23–28] Among various alloying elements, K. J. Park *et al.*[26] and H. C. Park *et al.*[27] stated that the addition of Cu acted as a sintering aid and facilitated greatly the densification of Ti_5Si_3 during PM process. Moreover, Kang *et al.*[28] reported that a thorough reaction among Ti, Si, and Cu by an explosive synthesis of elemental powders resulted in the formation of a single-phase Ti_5Si_3. In a previous study,[29] we investigated the influence of Cu addition on the CS of Ti_5Si_3 in Cu–Ti–Si system, and found that the morphologies of yielded products transformed from an obvious sintered–shaped coarse appearance to a cobblestone–like smooth surface. Interestingly, Cu serves not only as a diluent but also as a reactant that participates in the CS process. However, the exact reaction mechanism has not been clarified so far.

In this study, therefore, the principal objective is to explore the reaction pathway of CS of Ti_5Si_3 in Ti–Si systems with Cu addition. It is expected that the preliminary results could shed some light on the understanding of the reaction mechanism of Ti–Si system with a third metal addition.

II. Experimental Procedure

The starting materials in the present study are commercial powders of Cu (99.7% purity, ~45 μm), Ti (99.5% purity, ~15 μm), and Si (99.5% purity, ~15 μm). In Cu–Ti–Si system, the Ti and Si powders in a ratio corresponding to that of stoichiometric Ti_5Si_3 mixed with 0–50 wt% Cu were used as blended powders. Moreover, to study the interactions between each component in reactant mixtures, the Cu–Ti and Cu–Si systems were also prepared. The compositions of investigated systems are shown in Table I. All blended powders were mixed sufficiently by a ball-milling for 6 h. Differential thermal analysis (DTA) experiments were conducted using the thermal analysis apparatus (SDT–Q600; TA Ltd, New Castle, DE) with Al_2O_3 powders as the reference materials. A small amount of reactants weighing ~45 ± 1 mg was manually pressed into Al_2O_3 crucibles under flowing ultra high purity argon (100 ml/min) and heated at a rate of 30°C/min up to ~1200°C, except for some occasional interrupted runs to obtain the intermediate reaction products. Repeated experiments were conducted and the results with good repeatability were presented.

For Cu–Ti and Cu–Si systems, the temperature-time profiles were obtained from the samples heated in an electric resistance furnace (1.5 kW) under a protective atmosphere of high purity argon (5 L/min). Powder blends were uniaxially pressed into cylindrical compacts (6 mm in diameter and 6 ± 1 mm in length) under pressures ranging from 70 to 75 MPa to obtain green densities of 67 ± 2% theoretical density. Subsequently, the compacts were placed on the graphite-flat and heated at ~40°C/min to about 960°C. A thermocouple pair of W-5% Re vs W-26% Re (0.5 mm in

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Y. Zhao—contributing editor

Manuscript No. 31344. Received April 16, 2012; approved October 9, 2012.
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Table I. Reactant Compositions of the Investigated Systems

Designed composition	Cu (g)	Ti (g)	Si (g)
Ti_5Si_3	–	74.0	26.0
10 wt% Cu–Ti_5Si_3	10	66.6	23.4
30 wt% Cu–Ti_5Si_3	30	51.8	18.2
50 wt% Cu–Ti_5Si_3	50	37.0	13.0
Cu–Ti	30	51.8	–
Cu–Si	30	–	18.2

diameter) inserted into the hole (2 mm in diameter and half of the compact in length) drilled at the top of the compact was linked up with a temperature acquisition recorder to record the temperature-time curves.

The products retrieved from the DTA were analyzed for their phase compositions by X–ray diffraction (XRD, D/Max 2500PC; Rigaku Ltd, Tokyo, Japan) using Cu*K*α radiation. Microstructures of the fracture surface of DTA products were investigated by using field-emission scanning electron microscope (FESEM, FEIXL–30; FEI Ltd, Hillsboro, OR) equipped with an EDS analyzer (EDAX, SEDX–Genesis 2000; EDAX Inc, Mahwah, NJ).

III. Results and Discussion

(1) DTA Results of Cu–Ti–Si Systems

In the previous study,[29] we reported that addition of Cu to Ti–Si system significantly decreases the onset temperature of the reaction during DTA process. However, as the exact reaction mechanism of the Cu–Ti–Si system is still not clear so far, further research is continued in this study to reveal the exact reaction pathway.

Figure 1(a) and (b) show typical DTA curves and XRD patterns of DTA products of 0, 10, 30, and 50 wt% Cu–Ti–Si systems, respectively. For Ti–Si system, only one exothermic peak with an onset at ~871°C (near the transition temperature of α-Ti→β-Ti of 882°C) and a maximum at ~913°C emerges on the curve, indicating the reaction between Ti and Si is mainly dominated by the reaction of β-Ti and Si.

As for 10 wt% Cu–Ti–Si mixtures, an exothermic peak appeared at the temperature close to 804°C. Note that the onset temperature of ~795°C was much lower than that (~871°C) of the Ti–Si system, which suggested that the reaction could be greatly facilitated by the Cu addition. With further increase in temperature, a second exothermic hump with the peak appearing at ~894°C was observed, which was very close to that of the Ti–Si system. It is indicated that the ignition reaction in Ti–Si system was changed by 10 wt% Cu addition, whereas the combustion reaction was still dominated by the reaction between β-Ti and Si, as the Cu content is too meager to affect the whole exothermic reaction.

With 30 wt% Cu addition, surprisingly, a crossing feature appeared on the DTA trace with the onset of ~810°C [Fig. 1(a)]. According to our previous study,[29] the crossing feature was mainly attributed to the high exothermic reaction, leading to a rapid rise in the sample temperature, which, therefore, can be regarded as the CS reaction with a simultaneous combustion mode. Moreover, with 50 wt% Cu addition, the onset temperature of ~796°C was similar to those of 10 and 30 wt% Cu addition, and the exothermic peak appeared at the temperature near 813°C. In addition, when Cu content was increased over the range of 30–50 wt%, an endothermic peak appeared at ~1048°C–1052°C on the heating stage (solid lines) while an exothermic peak emerged at ~1034°C–1045°C on the cooling stage (dashed lines), corresponding to the melting and solidification of Cu, respectively.

According to XRD patterns [Fig. 1(b)], besides Ti_5Si_3, some intermediate phases (Ti_5Si_4, $TiSi_2$, and TiSi) and unreacted Ti are also detected in Ti–Si system, which suggests that the reaction in DTA apparatus tends to be incomplete without Cu addition. On the contrary, when reactions take place in 10–50 wt% Cu–Ti–Si systems, the products only consist of Ti_5Si_3 and Cu phases, without any transient phase, indicating that the reactions are complete.

Therefore, on the basis of the way of decreasing onset temperatures, we can see that the addition of Cu plays an important role in the CS of Cu–Ti–Si system, which could change the reaction pathway of Ti–Si system.

(2) Interrupted Experiments of Cu–Ti, Cu–Si, Ti–Si, and Cu–Ti–Si Systems

To determine phase formations and transitions in Cu–Ti–Si system, the binary Cu–Ti and Cu–Si systems with compositions

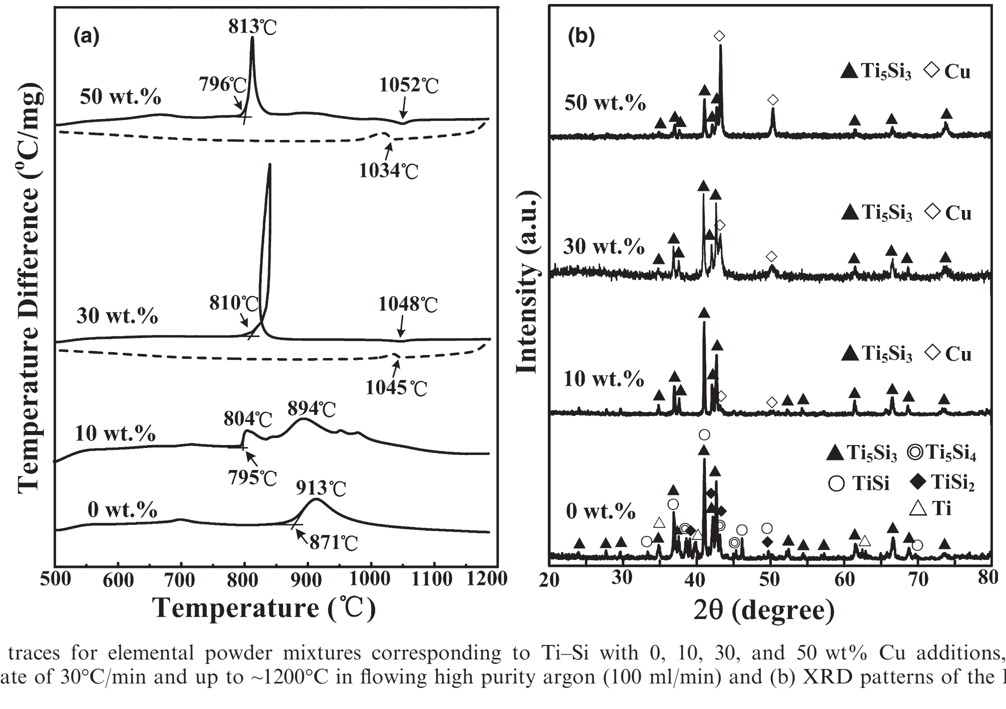

Fig. 1. (a) DTA traces for elemental powder mixtures corresponding to Ti–Si with 0, 10, 30, and 50 wt% Cu additions, respectively, at a constant heating rate of 30°C/min and up to ~1200°C in flowing high purity argon (100 ml/min) and (b) XRD patterns of the DTA products.

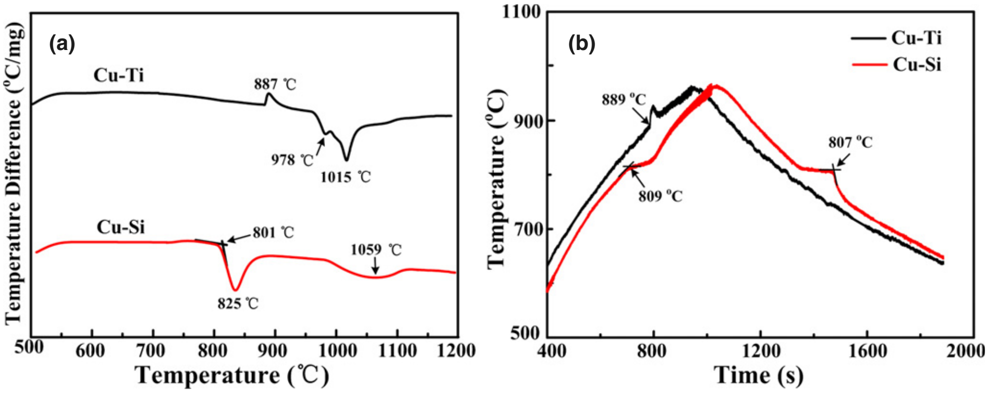

Fig. 2. (a) DTA traces of Cu–Ti and Cu–Si systems at a constant heating rate of 30°C/min and up to ~1200°C in flowing high purity argon (100 ml/min), (b) the temperature-time profiles for compacts corresponding to Cu–Ti and Cu–Si systems.

corresponding to 30 wt% Cu–Ti–Si system (Table I) were heated to ~1200°C in DTA apparatus, as shown in Fig. 2(a). For comparative purpose, the Cu–Ti and Cu–Si systems were also heated to ~960°C in an electric resistance furnace under flowing purity argon to obtain temperature-time profiles, as indicated in Fig. 2(b). Furthermore, based on onset temperatures of ~804°C–810°C in 10–50 wt% Cu–Ti–Si systems, a series of interrupted experiments were conducted for Cu–Ti, Cu–Si, Ti–Si and 30 wt% Cu–Ti–Si systems. The XRD patterns and FESEM micrographs of resultant products are shown in Figs. 3, 4, 5 and 6, respectively.

In Cu–Ti mixtures [Fig. 2(a)], an exothermic peak emerges at ~887°C, followed by two endothermic peaks at ~978°C and ~1015°C, respectively. Interestingly, the onset temperature of compacts in TE furnace was ~889 °C [Fig. 2(b)], which was close to the first reaction temperature (887°C) in the DTA [Fig. 2(a)], indicating that the reaction in TE furnace and DTA apparatus share some similarity. According to results of Liang *et al.*[30,31] complex reactions had occurred between Cu and Ti particles, as follows: after Cu–Ti mixtures were heated to ~887°C, the Ti_2Cu and TiCu phases were produced by solid–state diffusion reactions; subsequently, the Cu–Ti eutectic liquids were formed by reactions of Ti_2Cu and TiCu corresponding to the endothermic peak of ~978°C. Moreover, continuous heating could lead to the melting of Ti_2Cu into Cu–Ti liquids, corresponding to an endothermic peak of ~1015°C. Therefore, it is logical to conclude that the Cu–Ti and Cu–Ti–Si systems differ largely in reaction mechanisms.

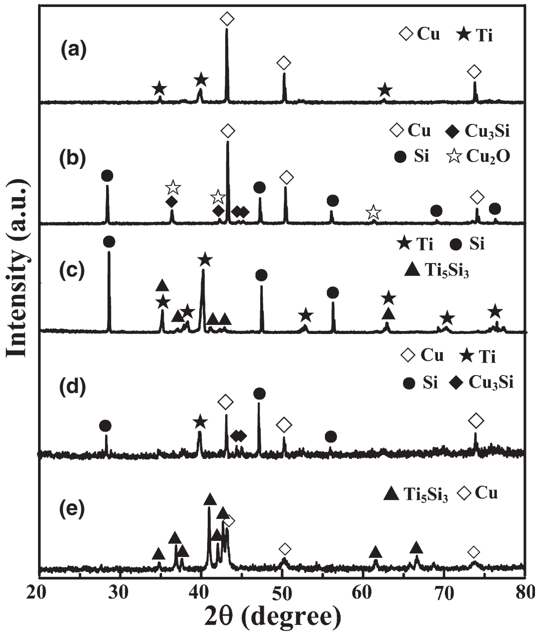

Fig. 3. XRD patterns of (a) Cu–Ti, (b) Cu–Si, (c) Ti–Si, and (d) 30 wt% Cu–Ti–Si mixtures in DTA interrupted at ~800°C as well as (e) 30 wt% Cu–Ti–Si mixtures in DTA interrupted at ~840°C.

From DTA traces of Cu–Ti system [Fig. 2(a)], no obvious reaction occurs below ~800°C, which is consistent with XRD pattern [Fig. 3(a)] and FESEM micrograph [Figs. 4(a) and (b)]. Compared with the raw powder mixture of Cu–Ti system [Fig. 4(a)], although the mixture is heated to 800°C, it is easy to distinguish between the cotton-like brightness particles of Cu and bulk-like gray particles of Ti [Fig. 4(b)]. Hence, we can deduce that the ignited reaction in Cu–Ti–Si system is independent of the Cu–Ti reaction.

In Cu–Si mixtures [Fig. 2(a)], there is one sharp endothermic peak with the onset at ~801°C and the minimum at ~825°C. From the XRD pattern of resultant products heated to ~800°C [Fig. 3(b)], we can observe that the Cu_3Si phase is detected besides unreacted Cu and Si phases. A small quantity of Cu_2O might be caused by the poor pressurization during DTA process. Furthermore, it can be observed clearly that some globular–like grains consisting of flake–white matrix and gray–striped phase were formed in the FESEM micrograph for the product heated to ~800°C [Fig. 4(c)]. The matrix of the grains mainly corresponds to Cu_3Si phases, as identified by EDS (e.g. point +1:74 at.% Cu and 26 at.% Si; point +2: 68 at.% Cu and 32 at.% Si; point +3:79 at.% Cu and 21 at.% Si), while the gray–striped phase located in the grains might be the Si phase (e.g., point +4:14 at.% Cu and 86 at.% Si; point +5:19 at.% Cu and 81 at.% Si; point +6:20 at.% Cu and 80 at.% Si). Moreover, the globular–like grain with smooth surface is a typical character of crystals formed by solidification from liquids. Note that the phase compositions in globular–like grain are in agreement with the Cu–Si phase diagram,[32] in which the Cu–Si eutectic liquids can be formed at 802°C (eutectic temperature) by the reaction of Cu_3Si and Si. Through diffusion couples of Cu–Si system annealed at 470°C for 8 h, Levin *et al.*[33] observed that the diffusion layer comprises the Cu_3Si phase solely. Consequently, it is rational to infer that during heating process, the Cu_3Si phase is produced initially by the solid-state diffusion reactions of Cu and Si, which further reacts with the remnant Si to form Cu–Si eutectic liquids at the onset of ~801°C. From Cu–Si profile [Fig. 2(b)], one can see that there are two temperature platforms on heating and cooling stages at ~807°C–809°C, respectively, which further confirm the formation of Cu–Si liquids.

For Ti–Si system [Fig. 1(a) 0 wt%], only one exothermic peak with an onset at ~871°C emerges on the DTA curve [Fig. 1(a) 0 wt%]. After heating reactants to 800°C, the

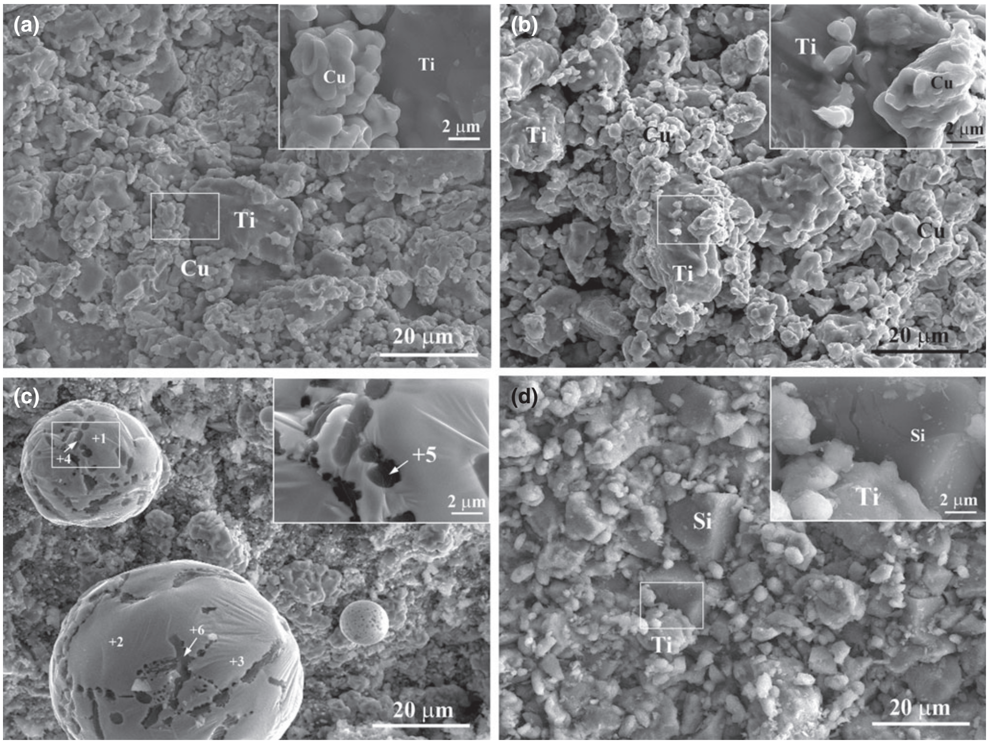

Fig. 4. Typical FESEM micrographs of the binary mixture in DTA (a) raw powder mixture of Cu–Ti mixture, (b) after heating to 800°C of Cu–Ti mixture, (c) after heating to 800°C of Cu–Si mixture, and (d) after heating to 800°C of Ti–Si mixture.

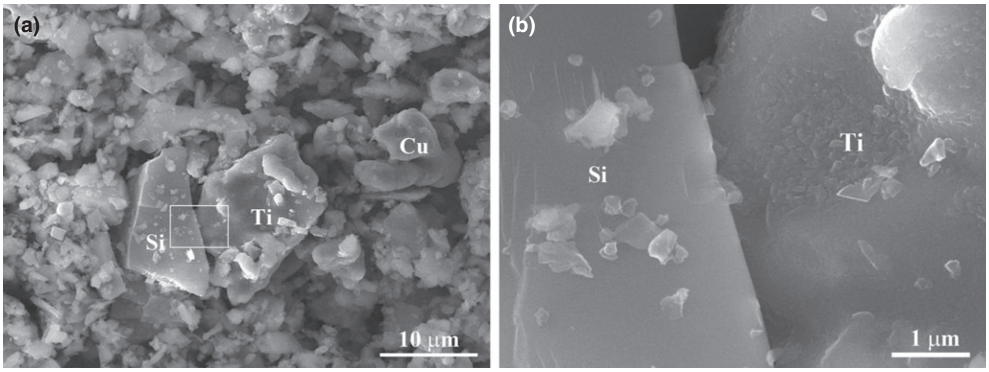

Fig. 5. (a) Typical FESEM micrographs of 30 wt% Cu–Ti–Si system after heating to 800°C in DTA, and (b) is the local magnification of the selected area in (a).

major phases detected are Ti and Si, together with a trace amount of Ti_5Si_3 phase [Fig. 3(c)]. According to the experiments of Ti–Si diffusion couples, Quenisset *et al.*[34] reported that slight Ti_5Si_3 phase could be detected in Ti–Si couples after being annealed at 600°C for 3 h. From microstructures of the mixture on heating to 800°C [Fig. 4(d)], it can be observed that the elemental Ti and Si are readily distinguished from each other, indicating that only slight reaction occurred between Ti and Si when the temperature reached to 800°C.

For 30 wt% Cu–Ti–Si system, when the heating run was stopped at ~800°C, the major products identified were remnant Cu, Ti, and Si phases, together with some amounts of Cu_3Si [Fig. 3(d)]. When the heating run was stopped at ~840°C, however, the dominant products became Ti_5Si_3 and Cu phases [Fig. 3(e)]. Microstructures for DTA products of Cu–Ti–Si system heated to 800°C and 840°C are shown in Figs. 5 and 6, respectively. After interruption at 800°C, the unreacted Cu, Ti, and Si can be easily identified [Figs. 5(a) and (b)], corresponding to the XRD analysis. After undergoing the exothermic event (840°C), one can see that the Ti_5Si_3 grains synthesized exhibit a cobblestone-like morphology with relatively smooth surface [Figs. 6(a) and (b)]. The morphology of Ti_5Si_3 grain agrees well with that of Ti_5Si_3 particulate synthesized by CS reaction.[29] Figs. 6(c) and (d) show the FESEM and back scattering electron (BSE) images, respectively, for the same viewing field, which clearly indicates the bonding agents of Cu phase distribute in boundaries of Ti_5Si_3 grains.

To estimate the reaction temperature of Cu–Ti–Si system during CS process, we calculate the adiabatic combustion temperature (T_{ad}). It is supposed that the possible reactions in Cu–Ti–Si system can be summarized as an overall reaction:

$$x\mathrm{Cu} + \frac{5}{8}(1-x)\mathrm{Ti} + \frac{3}{8}(1-x)\mathrm{Si} \rightarrow x\mathrm{Cu} + \frac{1}{8}(1-x)\mathrm{Ti_5Si_3} \quad (1)$$

According to Eq. (1), the T_{ad} of the Cu–Ti–Si system can be calculated based on the relationship given by Moore and

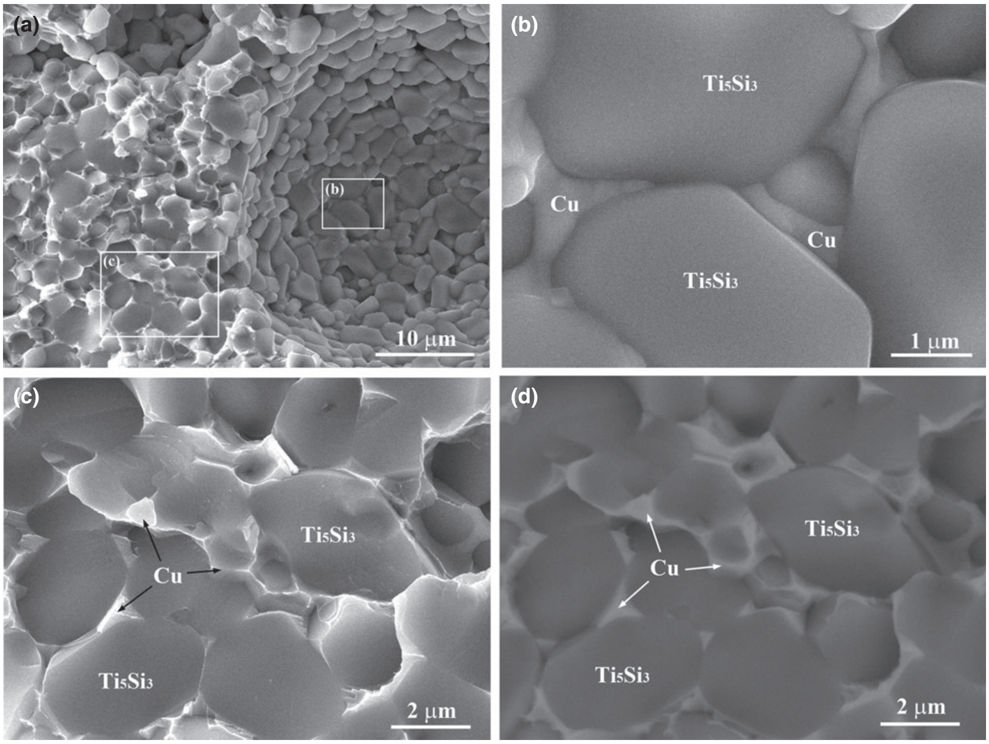

Fig. 6. (a) Typical FESEM micrographs of 30 wt% Cu–Ti–Si system after heating to 840°C in DTA, (b) and (c) are the local magnifications of the selected area in (a), respectively, and (d) BSE image of (c).

Feng,[35] which assumes that the propagating mode is initiated at a certain temperature of T_0, as shown in Eq. (2).

$$\sum_{\mathrm{k}} n_{\mathrm{k}} \Delta H_{\mathrm{f},T_0} + \sum_{\mathrm{j}} n_{\mathrm{j}} \int_{T_0}^{T_{\mathrm{ad}}} C_{\mathrm{P}}(P_{\mathrm{j}}) \cdot \mathrm{d}T + \sum_{\mathrm{j}} n_{\mathrm{j}} L(P_{\mathrm{j}}) = 0 \quad (2)$$

where $\Delta H_{\mathrm{f},T_0}$ is the formation enthalpy at T_0; $C_{\mathrm{P}}(P_{\mathrm{j}})$ and $L_{\mathrm{P}}(P_{\mathrm{j}})$ are the heat capacity and phase transformation enthalpy (if the products go through a phase change, e.g., solid to liquid or liquid to gas) of the products, respectively; n_{k} is the stoichiometric coefficient of Eq. (1), while n_{j} is the stoichiometric coefficient of the products (P_{j}); and T_{ad} refers to the adiabatic combustion temperature.

According to Fig. 1(a), the preheat temperature is selected as T_0 = 1073 K (800°C), and the calculated result of Eq. (2) is shown in Fig. 7. Except for two plateaus (horizontal lines), one can see that the T_{ad} value decreases with the increase in Cu content (Fig. 7). Note that the two plateaus with Cu contents ranging from 11.0 to 43.5, and 82.2 to 92.3 wt% correspond to melting points of Ti_5Si_3 (2403 K) and Cu (1357 K), respectively. During the melting process (phase transition), the T_{ad} value remains constant despite of the increase in Cu content. It can be seen that the 30 wt% Cu–Ti–Si system corresponds to the T_{ad} of 2403 K (2130°C), which is equal to the melting point of Ti_5Si_3, but significantly higher than those of Ti (1933 K), Si (1685 K), and Cu (1357 K). Therefore, it is rational to believe that as the reaction zone propagated as a wave front through the sample, the reactants would convert to liquids driven by the exothermicity of the reaction, which favors the precipitation of Ti_5Si_3 particulates. Moreover, the cobblestone-like morphology with relatively smooth surface of Ti_5Si_3 grains (Fig. 6) is also a typical feature of crystal precipitated out of oversaturation of liquids.[29]

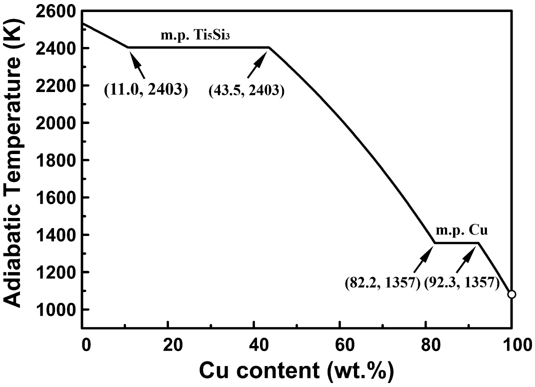

Fig. 7. Effect of Cu content on the combustion temperature of Cu–Ti–Si system with a preheat temperature of 1073 K (800°C).

As reported by He and Stangle,[36] the CS reaction begins with an ignition process, in which at least a portion of the sample's surface is exposed to an external heat source for a short time, to generate a self–propagating combustion wave front that passes through the sample. Nevertheless, based on the above analysis, it can be observed that neither in the Ti–Si [Fig. 1(a)] nor in the Cu–Ti [Fig. 2(a)] system did exothermic reactions occur evidently although the samples were heated to ~800°C. For Cu–Si system [Fig. 2(b)], instead of development of heat, the endothermic reaction absorbed a large quantity of heat from the surroundings. So the ignition reaction of Cu–Ti–Si system is not that of the binary mixtures of Ti–Si, Cu–Ti, and Cu–Si systems.

Combining the results of Figs. 1, 2 and 3, we suggest that the reaction between Cu–Si eutectic liquids and Ti triggers the combustion reaction in Cu–Ti–Si system. In other words, adding Cu to the Ti–Si system would result in the formation of Cu–Si eutectic liquids prior to the α-Ti→β-Ti transition, which changes the ignition reaction mechanism and, therefore, is much indispensable for the CS of Cu–Ti–Si system.

(3) Reaction Pathway in Cu–Ti–Si System

On the basis of aforementioned results, a model illustrating the reaction pathway is proposed in the 30 wt% Cu–Ti–Si

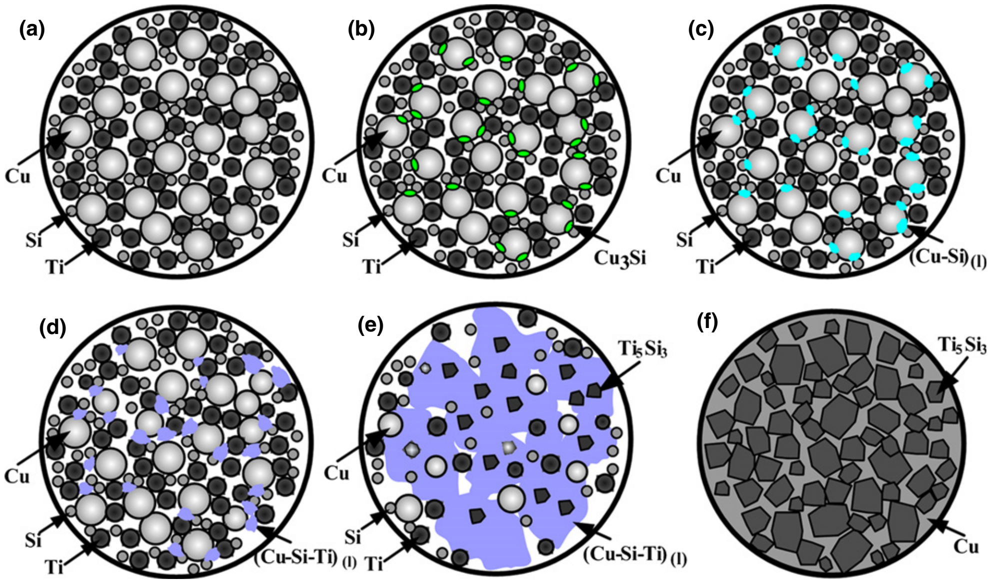

Fig. 8. A model illustrating the reaction pathway of combustion synthesis (CS) in Cu–Ti–Si system.

system during CS, as shown in Fig. 8(a)–(f). With the increase in temperature, the compound Cu_3Si was formed initially via a sluggish solid-state diffusion reaction between Cu and Si particles [Fig. 8(b)], and then the continuous heating further promoted Cu_3Si and Si to form Cu–Si eutectic liquids at ~802°C [Fig. 8(c)]; simultaneously Ti was dissolved into the surrounding Cu–Si binary liquids and led to the formation of Cu–Ti–Si ternary liquids [Fig. 8(d)]. Once the liquids reached a saturation stage with [Ti] and [Si] in the course of continuous dissolution, the Ti_5Si_3 precursors were precipitated out of the Cu–Ti–Si liquids, leading to an abrupt increase in temperature and thus initiating the combustion reaction [Fig. 8(e)]. The heat generated by the reaction significantly promoted more Ti and Si dissolved into the liquids, making the Cu–Ti–Si liquids sufficiently supersaturated quickly, and then plenty of Ti_5Si_3 could be developed from the liquids by a solution–reaction–precipitation mechanism with the continual consumption of [Ti] and [Si] [Fig. 8(f)]. In short, the reaction pathway could be described briefly as: $Cu_{(s)} + Ti_{(s)} + Si_{(s)} \rightarrow Cu_3Si_{(s)} + Ti_{(s)} + Si_{(s)} \rightarrow (Cu\text{–}Si)_{(l)} + Ti_{(s)} \rightarrow (Cu\text{–}Ti\text{–}Si)_{(l)} \rightarrow Cu_{(l)} + Ti_5Si_{3(s)}$. Finally, unlike the Ti–Si system, the reaction was complete with the addition of Cu and the final products only contained Ti_5Si_3 and Cu stable phases without any intermediate phases.

When 10 wt% Cu was added to Ti–Si system, the yielded Cu_3Si was insufficient to form enough Cu–Si and Cu–Ti–Si liquids, resulting in the precipitation of a small amount of Ti_5Si_3 out of the liquids. Consequently, the released heat, corresponding to the exotherm of ~804°C [Fig. 1(a)], could not ignite the whole combustion reaction. As a result, the CS was still dominated by the reaction between β-Ti and Si, corresponding to the exotherm of ~894°C. As the Cu content was further increased to 50 wt%, however, the heat of absorption was also increased by excessive Cu, leading to the disappearance of crossing feature in DTA curves, corresponding to the exotherm of ~813°C [Fig. 1(a)].

Furthermore, it is interesting to note that there is a large difference between Cu–Ti–Si system and Cu–Ti–C system. According to the results reported by Liang *et al.*[30,31], the solid-state reaction occurred firstly between metallic Cu and Ti phases, followed by the formation of Cu–Ti eutectic liquids, and then the nonmetallic C dissolved into binary liquids forming Cu–Ti–C liquids. However, in this study, the solid-state reaction took place initially between metallic Cu and nonmetallic Si, followed by the production of Cu–Si eutectic liquids; subsequently the metallic Ti was dissolved into binary liquids forming Cu–Ti–Si liquids.

Therefore, the addition of Cu to Ti–Si system thoroughly changed the reaction pathway by the prior formation of binary Cu–Si and ternary Cu–Ti–Si liquids during CS, which provides an easier route for the reactant transfer and accelerates the occurrence of complete reaction.

IV. Conclusions

The addition of Cu to Cu–Ti–Si system significantly promotes the reaction between Ti and Si by the prior formation of Cu–Si and Cu–Ti–Si liquids, which provides an easy route for reactant transfer and accelerates the occurrence of complete reaction. The reaction pathway of 30 wt% Cu–Ti–Si system during CS could be described as: the Cu_3Si was formed initially via solid-state diffusion reaction between Cu and Si particles; with the temperature increasing, Cu–Si eutectic liquids were formed at ~802°C between Cu_3Si and Si; then Ti was dissolved into the surrounding Cu–Si liquids and led to the formation of Cu–Ti–Si ternary liquids; meanwhile, once the liquids reached a saturation stage with [Ti] and [Si] in the course of continuous dissolution, the Ti_5Si_3 precursors were precipitated out of the Cu–Ti–Si liquids, leading to an abrupt increase in temperature and thus initiating the combustion reaction. The heat generated by the reaction significantly promoted more Ti and Si to dissolve into the liquids, making the Cu–Ti–Si liquids sufficiently supersaturated quickly, and finally plenty of Ti_5Si_3 could be developed from the liquids by a solution–reaction–precipitation mechanism with the continual consumption of [Ti] and [Si].

Acknowledgment

This work is supported by The National Science Foundation of China (no. 50671044), The National Basic Research Program of China (973 Program) (no. 2012CB619600) and Foundation of Jilin University for Distinguished Young Scholars.

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