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Evolution process of the synthesis of TiC in the Cu–Ti–C system

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Abstract

The evolution process of TiC formation in the 20 wt.% Cu–Ti–C powder mixtures was studied by using differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The Ti_xCu_y compounds (Ti_2Cu, TiCu, Ti_3Cu_4 and $TiCu_4$) formed initially via solid-state diffusion reactions between Cu and Ti particles; and then Ti_2Cu and TiCu can form a Cu–Ti eutectic liquids at about 1233 K. The unreacted Ti and C particles dissolved into the Cu–Ti liquids and led to the formation of Cu–Ti–C ternary liquids; subsequently, TiC particulates precipitated out of the saturated liquids. At the same time, also the formation of Ti_2Cu occurred at the interface between the Cu–Ti liquids and the unreacted Ti particles. As the temperature increased further, the Ti_2Cu melted and more Cu–Ti liquids formed; and then C particles continuously dissolved into the Cu–Ti–C liquids and TiC particulates gradually precipitated out of the saturated liquids.

Keywords: Titanium carbide; Differential thermal analysis; Copper; Evolution process

1. Introduction

Good electrical and thermal conductivity, in addition to chemical stability, make copper an attractive material for a wide range of applications such as power industry, electric industry and engineering industry [1,2]. However, pure copper possesses the lower strength and is a soft metal, which can easily lead to premature failure of components in the service. Therefore, the widespread use of copper is limited. The methods to improve its properties and retain its high thermal conductivity are a major challenge. Ceramic particulate reinforced Cu matrix composites have attracted wide interest in recent years [3,4]. These materials exhibit a combination of the excellent thermal and electrical conductivities, high strength retention at elevated temperatures, and high microstructural stability [4].

Titanium carbide, because of its high modulus, hardness and melting temperature, is an attractive compound for use as a reinforcing phase in metallic matrices. Recently, TiC particulate reinforced Cu matrix composites have been extensively investigated by such processing techniques as self-propagating high-temperature synthesis (SHS) [5–7], powder metallurgy [8], preform infiltration [9] and casting techniques [10]. Among these fabrication technologies, the SHS technology was attached to much attention, due to its low energy consumption, high time efficiency and high product purity [11]. However, due to the high combustion temperature and extremely fast velocity of the SHS reaction, knowledge of the microscopic reaction mechanisms involved in these processes is still quite limited [12].

Titanium carbide can be produced by SHS reaction between mixtures of Ti and C powders. The ignition temperature for this reaction is close to the melting point of Ti [13]. However, in the Ti–C system, the melting point of Ti was so high that excessive energy was consumed. Therefore, through the addition of a metallic powder, a low melting point eutectic can be produced in the initial stages of the reaction, facilitating ignition well below the melting point of Ti [14]. The Cu–TiC composites including 20–80 vol.% TiC were fabricated using SHS reaction by Kwon et al. [7]. The combustion reaction between Ti and C initiated near the melting point of pure Cu, suggesting that the reaction is initiated by the formation of liquid Cu.

However, the combination of high reaction temperatures and high propagation rates of SHS process makes it difficult to investigate experimentally such reactions using conventional techniques applied in solid-state reactivity studies. The lack of knowledge of the reaction mechanism makes difficult to anticipate the ignition behavior of the reactions. Although the

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information obtained from the DTA experiments is incomplete, it is valuable to help understanding the ignition behavior in the SHS reaction. The objective of this study is to determine the evolution process of the synthesis of TiC in the 20 wt.% Cu–Ti–C system using differential thermal analysis (DTA) and X-ray diffraction (XRD). It is expected that the preliminary results can be significant in promoting the understanding of SHS process in the Cu–Ti–C system.

2. Experimental procedure

The starting materials were made from commercial powders of Cu (99.0%, particle size less than 6 μm), titanium (99.5%, particle size less than 15 μm) and carbon (99.9%, particle size less than 38 μm). In order to provide an insight into the evolution process of TiC formation, the interactions between each components in the 20 wt.% Cu–Ti–C (with a molar ratio of Cu:Ti:C = 1:4.27:4.27), Cu–Ti (with a molar ratio of Cu:Ti = 1:4.27),Cu–C (with a molar ratio of Cu:C = 1:4.27) and Ti–C system (with a molar ratio of Ti/C = 1:1) were also studied by DTA. It was noted the Ti–C, Cu–C and Cu–Ti system correspond to the same atomic proportion as that in the mixtures of Ti/C = 1:1 mixed with 20 wt.% Cu, respectively.

DTA experiments were performed using the Model Rigaku-8150 (Japan) apparatus. For DTA studies, 50 mg samples of reactant mixtures were prepared and placed in alumina sample crucibles. DTA was conducted from room temperature to 1473 K at a heating rate of 40 K/min in flowing high purity argon gases. DTA temperature calibrations were made using aluminum (in argon) standards heated at 40 K/min. All temperature data were shifted based on linear interpolation to literature values for the melting points of these standards 933.4 K. The samples retrieved from the DTA were ground in an alumina mortar and analyzed using XRD (Model D/Max 2500PC Rigaku, Japan). Microstructures of the fracture surface of the DTA products were investigated by using scanning electron microscopy (SEM) (JSM6360-LV Japan) equipped with energy-dispersive spectrometer (EDAX).

3. Results and discussion

3.1. Thermodynamics

During the exothermic reactions in powder mixtures, Ti, C, and Cu may interact to form some possible products due to the existence of the following chemical reactions.

$$\tfrac{1}{2}\mathrm{Ti}+\tfrac{1}{2}\mathrm{C}\rightarrow\tfrac{1}{2}\mathrm{TiC},\qquad G_1^0=-92400+6.275T\ \mathrm{J/mol}\qquad(1)$$

$$\tfrac{2}{3}\mathrm{Ti}+\tfrac{1}{3}\mathrm{Cu}\rightarrow\tfrac{1}{3}\mathrm{Ti_2Cu},\qquad \Delta G_2^0=-12131+4.688T\ \mathrm{J/mol}\qquad(2)$$

$$\tfrac{1}{2}\mathrm{Ti}+\tfrac{1}{2}\mathrm{Cu}\rightarrow\tfrac{1}{2}\mathrm{TiCu},\qquad \Delta G_3^0=-11206+3.272T\ \mathrm{J/mol}\qquad(3)$$

$$\tfrac{3}{7}\mathrm{Ti}+\tfrac{4}{7}\mathrm{Cu}\rightarrow\tfrac{1}{7}\mathrm{Ti_3Cu_4},\qquad \Delta G_4^0=-9748+2.278T\ \mathrm{J/mol}\qquad(4)$$

$$\tfrac{1}{5}\mathrm{Ti}+\tfrac{4}{5}\mathrm{Cu}\rightarrow\tfrac{1}{5}\mathrm{TiCu_4},\qquad \Delta G_5^0=-6011+2.339T\ \mathrm{J/mol}\qquad(5)$$

In order to determine the reaction directions and the synthesized products, the reaction standard Gibbs free energies ΔG^0 of the Eqs. (1)–(5) were theoretically calculated according to the thermodynamics data [15,16], and the results are shown in Fig. 1. It can be observed that the changes in standard Gibbs free energies of five reactions are all negative, which indicates the above reactions are all favorable. It is worth noting that ΔG_1^0 is more negative for the formation of TiC among the five possible products, and thus the reaction (1) has a higher tendency for the formation of TiC than the other four reactions. Therefore, it can be deduced that the TiC is the most stable phase in the exothermic reaction products of the Cu–Ti–C system.

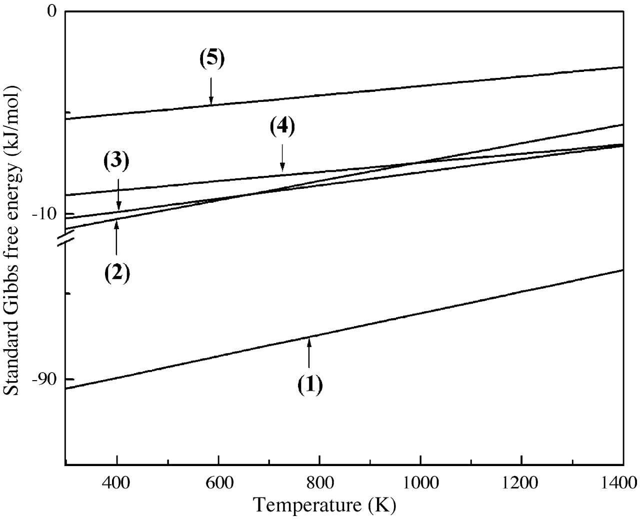

Fig. 1. Change of standard Gibbs free energy as the temperature for Eqs. (1)–(5).

3.2. Differential thermal analysis

Fig. 2 shows the DTA curves of the reactant mixtures from the Cu–Ti–C, Cu–Ti, Cu–C, and Ti–C systems, respectively. For the Ti–C mixtures heated to 1473 K, the DTA result indicates that no evidently exothermic reaction had occurred. In the DTA curve of the Cu–C system, there was only one endother-

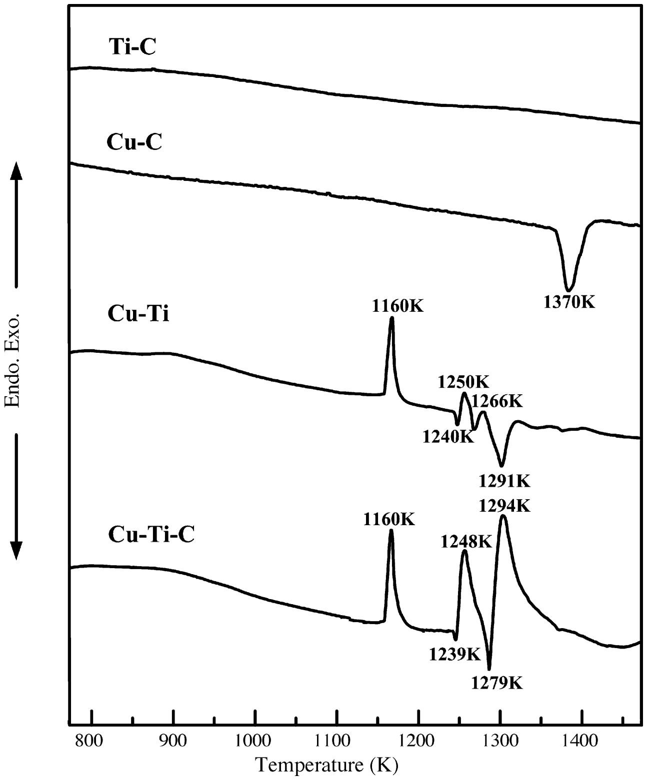

Fig. 2. DTA curves for various compositions heated in argon environments at a heating rate of 40 K/min to 1473 K.

mic peak with the minimum at 1370 K, which corresponds to the melting of Cu. Based on the binary Cu–C phase diagram [17], the Cu–C system comprises no stoichiometric compounds and only limited solubility in the existing phases, i.e., carbon dissolves only to limited amounts in Cu and vice versa. This is further supported by the fact that the mutual solubility of Cu and C is low in combination with the absence of an intermediate compound [17]. The binary Cu–Ti system is a complex system in which the several different compounds exist [18,19]. From DTA curve of the Cu–Ti system, it can be observed that three exothermic peaks with the maximum at 1160, 1250, and 1266 K as well as two endothermic peaks with the minimum at 1240 and 1291 K appeared, respectively. The reaction products of the Cu–Ti powder mixtures were analyzed by XRD and the results were presented in Fig. 3. From Fig. 3, it was indicated that, after heating the Cu–Ti powder mixtures to 1023 K, a large quantity of Cu and Ti phases were detected. The results showed that obviously the exothermic reaction between Cu and Ti mixtures did not occurred before 1023 K. When the temperature increased to 1123 K, a small quantity of Ti_2Cu, TiCu, Ti_3Cu_4 and $TiCu_4$ were detected but the unreacted starting powders. It was indicated that a relatively slow solid-state diffusion reaction had occurred between Cu and Ti particles, although the DTA curve showed no significantly exothermic peak. Therefore, the slow solid-state diffusion reaction corresponding to Eqs. (2)–(5) had occurred. When this mixture was heated to 1160 K, a large quantity of Ti_2Cu, TiCu and Ti as well as a small quantity of Cu were identified by XRD, while the Ti_3Cu_4 and $TiCu_4$ peaks disappeared. According to the result of the calculation of Gibbs free energies (Fig. 1), it can be seen that the ΔG_2^0 and ΔG_3^0 of the reactions between Cu and Ti to form Ti_2Cu and TiCu are more negative than ΔG_4^0 and ΔG_5^0 of the reactions between Cu and Ti to form Ti_3Cu_4 and $TiCu_4$. Therefore, the further reaction may occur between Ti_3Cu_4 and Ti, and $TiCu_4$ and Ti to form more stable Ti_2Cu or TiCu.

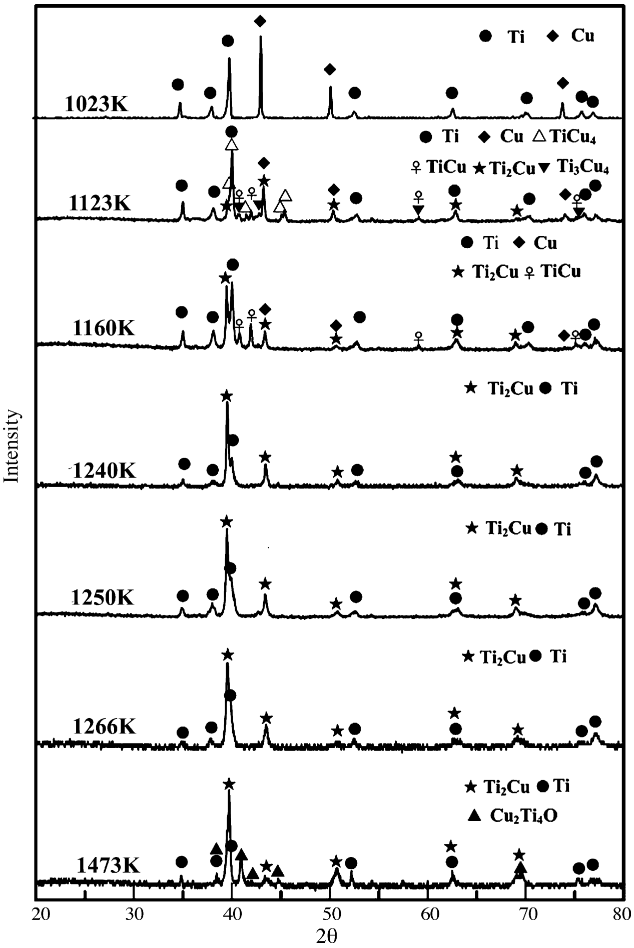

Fig. 3. XRD patterns of the DTA products synthesized by the Cu–Ti system quenched at 1023, 1123, 1160, 1240, 1250, 1266, and 1473 K, respectively.

With the increasing of the temperature, one slightly endothermic peak with the minimum at 1240 K was observed in the DTA curves of the Cu–Ti system. According to the Cu–Ti phase diagram [18], it can be seen that there are two eutectic reaction temperatures of 1148 K and 1233 K, respectively. Closer to the titanium-rich side of the phase diagram a eutectic point (1233 K) is found in which TiCu and Ti_2Cu precipitates. Therefore, during the solid diffusion reaction process between Cu and Ti mixtures, once the temperatures reached to the eutectic point of Ti_2Cu and TiCu, the Cu–Ti eutectic liquids formed quickly. For the Cu–Ti powder mixtures heated to 1240 K, the products of Ti_2Cu and Ti were detected, while no TiCu was found. In this case, TiCu together with Ti_2Cu may form Cu–Ti eutectic liquids, corresponding to the endothermic peak with the minimum at 1240 K in the DTA curves. At the same time, the local formation of Cu–Ti eutectic liquid as well as unreacted Ti and Cu particles subsequently started to dissolve into the eutectic liquids, leading to the formation of Cu–Ti liquids, and then Ti_2Cu was formed during the following solidification. Therefore, the Ti_2Cu in reaction products at 1240 K may be formed both from the diffusion reaction between solid Cu and solid Ti mixtures and from the solidification process of Cu–Ti liquids. However, it should be mentioned that the TiCu could not be detected in the XRD, which may be due to its low content. Moreover, the corresponding XRD result showed that the no Cu diffraction peak is found in the products at 1240 K, and it may be exhausted during the formation of Ti_xCu_y compounds and Cu–Ti liquids.

At the heating temperature of 1250 K, the identified phases were Ti_2Cu and Ti in the products. After Cu–Ti liquids formed at the local region, the Cu–Ti liquids spread over the unreacted Ti particles, leading to the formation of Ti_2Cu at the interface between the Cu–Ti liquids and the Ti particles. Ti continued to dissolve into the Cu–Ti liquid solution by diffusion across the product Ti_2Cu layer to form Ti_2Cu. Thus, the exothermic peak with the maximum at 1250 K in the DTA curves was observed because of the formation of Ti_2Cu at the interface between the Cu–Ti liquids and the Ti particles. When the mixtures were heated to 1266 K, the composition of products did not change, indicating the exothermic reaction of 1266 K corresponding to the continuous formation of Ti_2Cu at the interface region. With the temperature further increased, the heat released from exothermic reactions of the mixtures and continuous heating can lead to the melting of Ti_2Cu into Cu–Ti liquids, corresponding to the endothermic peak at 1291 K in the DTA curves. After heating the mixtures to 1473 K, a large number of Ti_2Cu and Ti were identified except only a small quantity of Cu_2Ti_4O caused by the poor pressurization of the DTA apparatus during the following solidification.

For the 20 wt.% Cu–Ti–C mixtures heated to 1473 K, three strong exothermic peaks with the maximum at 1160, 1248, and 1294 K as well as two endothermic peaks with the minimum at 1239 and 1279 K appeared in the DTA curves (Fig. 2), respectively. It can be seen clearly that one exothermic peak with the maximum at 1160 K and one endothermic peak with the minimum at 1239K were significantly similar to the Cu–Ti system. The result suggested that the Cu–Ti reactions to form Ti_xCu_y compounds were more favourable than the Cu–C and Ti–C reactions in the Cu–Ti–C system in the temperature range of the present study. The XRD results of the DTA products after the different heated temperature of the 20 wt.% Cu–Ti–C powder mixtures were shown in Fig. 4. When the 20 wt.% Cu–Ti–C mixture was heated to 1123 K, in addition to the unreacted Cu, Ti, and C phases, a small quantity of Ti_2Cu, TiCu, and $TiCu_4$ were found. Compared with the XRD results of the Cu–Ti mixture heated to 1123 K, no Ti_3Cu_4 phase was detected, which suggested that the presence of C may restrain the solid-state diffusion reactions at the interface between the Cu and Ti particles. After heating the mixtures to 1160 K, a large quantity of Ti_2Cu and TiCu were detected but the unreacted starting powders, as shown in Fig. 4, which was very analogy with the results in the Cu–Ti system.

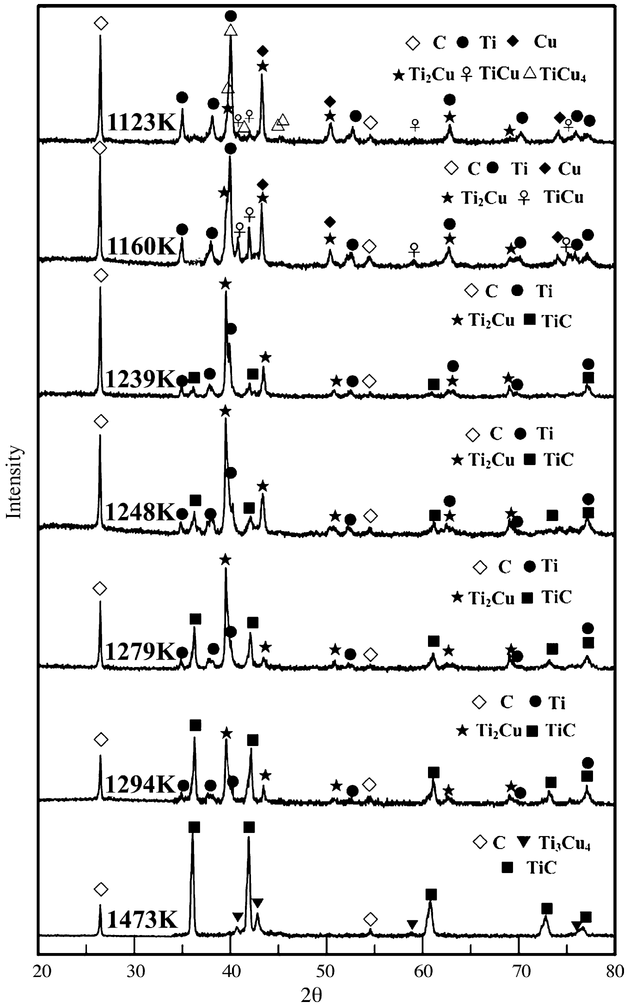

Fig. 4. XRD patterns of the DTA products synthesized by the 20 wt.% Cu–Ti–C system quenched at 1123, 1160, 1239, 1248, 1279, 1294, and 1473 K, respectively.

After heating the mixtures to1239 K, one slightly endothermic peak was observed in the DTA curves of 20 wt.% Cu–Ti–C system. The corresponding XRD result showed that a large quantity of Ti_2Cu and a trace amount of TiC were detected but this unreacted the starting powders. When the temperature reached to the eutectic point (1233 K) of Ti_2Cu and TiCu, the Cu–Ti eutectic liquids quickly formed and spread over the unreacted Ti and C particles. The Ti and C particles dissolved into the Cu–Ti liquids and led to the formation of the Cu–Ti–C ternary liquids; subsequently, TiC particulates precipitated out of the saturated liquids. Therefore, the initial temperature of the reaction of TiC formation could be prophesied at about 1233 K in the 20 wt.% Cu–Ti–C system.

At the same time, the reaction between Ti and C as well as the formation of Ti_2Cu at the interface between the Cu–Ti–C liquids and the unreacted Ti particles were also followed. When the temperature continued to be increased to 1248 K, the products did not change, however, the XRD peak of TiC became stronger, indicating the broad exothermic peak with the maximum at 1248 K corresponding to the continuous formation of TiC and Ti_2Cu. When the temperature increased further, the Ti_2Cu melted into Cu–Ti liquids, which was indicated that the endothermic peak with the minimum at 1279 K in the DTA curves. For the mixtures heated to 1279 K, the products consisted of TiC, Ti_2Cu and Ti phases, while Ti_2Cu were formed during the following solidification process. After melting of Ti_2Cu, more Cu–Ti liquids formed and spread over the C particles. Carbon particles continuously dissolved into the Cu–Ti–C liquids, as a result, TiC particulates gradually precipitated out of the saturated liquids. Therefore, a large quantity of TiC were formed, which corresponded to the exotherm of 1294 K in the DTA curves. When the temperature increased to 1473 K, a large quantity of TiC, Ti_3Cu_4 formed, and a small quantity of C remained, indicating that the conversion of Ti and C to form TiC was uncompleted. It may be the reason that the volume of DTA sample is much smaller, and therefore, the heat released by the reactions may dissipate into the surroundings more easily, resulting in an incomplete reaction. It should be noted that no Cu diffraction peak is found in the final products, and it may exist in the form of Ti_3Cu_4. Furthermore, the Cu content in the reactants plays a significant role in promoting the occurrence of ignition and the effect of Cu content is being further investigated in our group.

3.3. Microstructural evolution

To develop a deeper understanding of the TiC formation of the 20 wt.% Cu–Ti–C mixtures in DTA, the typical back scatter images of the raw powder and products at various temperature of 1160 K, 1248, 1279, 1294, and 1473 K are shown in Figs. 5(a)–(f), respectively. Microstructure observation was in agreement with the XRD identification results. Fig. 5(a) shows

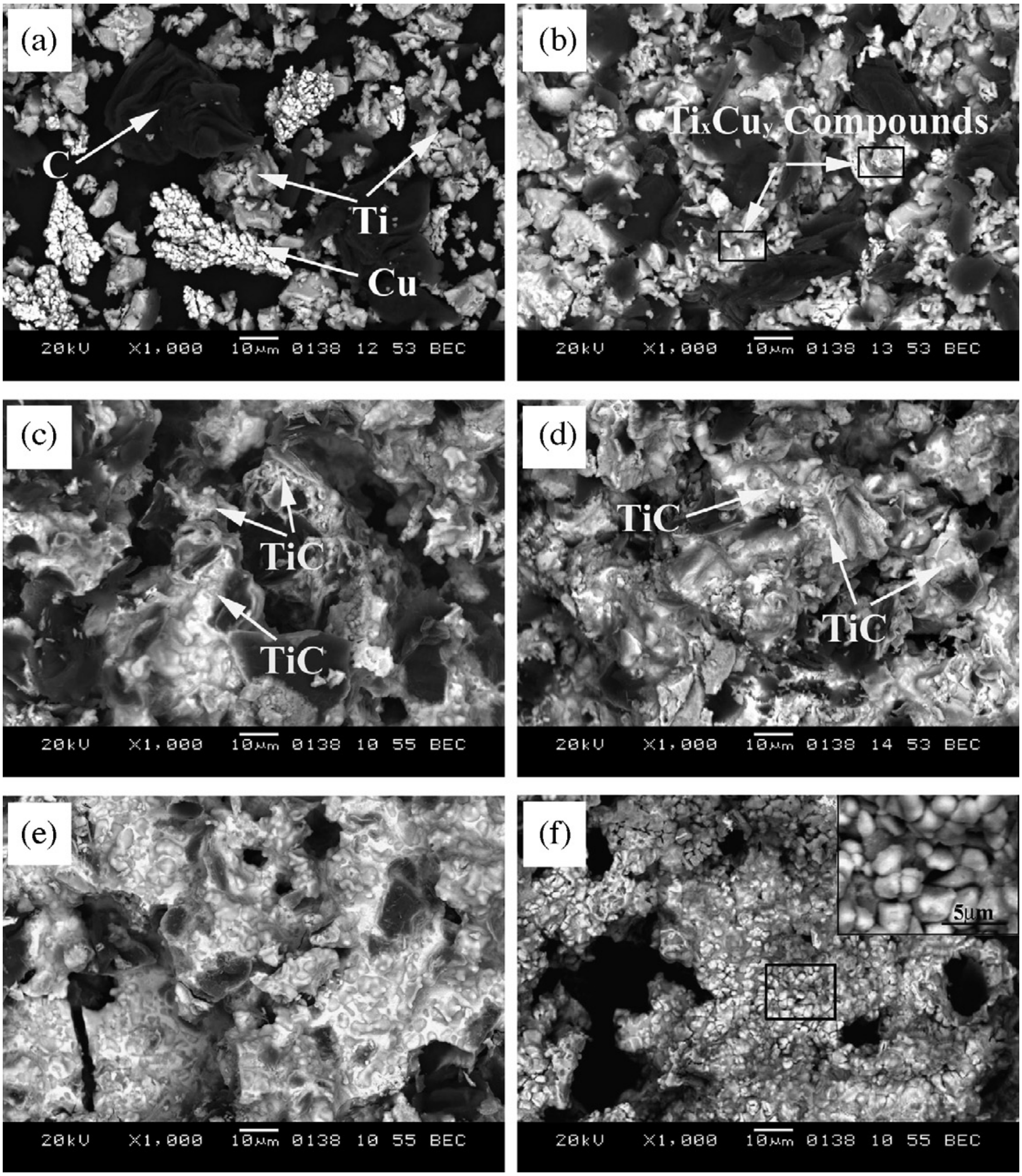

Fig. 5. Back scatter images of the DTA products synthesized by the 20 wt.% Cu–Ti–C system at (a) room temperature, quenched at (b) 1160 K, (c) 1248 K, (d) 1279 K, (e) 1294 K, and (f) 1473 K, respectively.

a back scatter image of the raw powder, where the dark areas represent the starting C particles, and the gray areas represent Ti particles and the bright areas represent Cu particles. After heating the mixtures to 1160 K, a large quantity of Ti_xCu_y compounds were detected in the products, as shown in Fig. 5(b). Fig. 5(c) shows the typical microstructures of the products at 1248 K, it can be observed that the Cu–Ti liquids formed and spread over the unreacted Ti and C particles. Thus, the Ti and C particles dissolved into the Cu–Ti liquids and led to the formation of the Cu–Ti–C ternary liquids. It can be seen that many small TiC particles were precipitated out of the liquid regions. Figs. 5(d), (e), and (f) show the typical microstructures of the products at 1279, 1294, and 1473 K, respectively. Clearly, with the temperature increasing, C particles became smaller and were continuously consumed, and then TiC particulates were gradually precipitated out of the saturated liquids.

4. Conclusions

Based on the DTA and XRD results of the Cu–Ti, Cu–C, Ti–C, and Cu–Ti–C systems, the evolution process of TiC formation may be described as follows: the Ti_xCu_y compounds (Ti_2Cu, TiCu, Ti_3Cu_4, and $TiCu_4$) formed initially via the solid-state diffusion reactions between the Cu and Ti particles; and then the Ti_2Cu and TiCu can form the Cu–Ti eutectic liquids at about 1233 K. The unreacted Ti and C particles dissolved into the Cu–Ti liquids and led to the formation of the Cu–Ti–C ternary liquids; subsequently, TiC formed in the liquids. At the same time, the formation of Ti_2Cu occurred at the interface between the Cu–Ti liquids and the unreacted Ti particles. When the temperature increased further, the Ti_2Cu melted and more Cu–Ti liquids formed; and then C particles continuously dissolved into the Cu–Ti–C liquid and TiC particulates gradually precipitated out of the saturated liquids. Therefore, the initial temperature of the reaction of TiC formation could be prophesied at about 1233 K in the 20 wt.% Cu–Ti–C system.

Acknowledgements

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