1. Introduction

Metal matrix composites (MMCs) dispersed with discontinuous particulates gain a considerable amount of attention as an important engineering material in automotive, aerospace and defence sectors and also to an extent in general engineering because of their improved properties (low density, excellent castability, good wear resistance and fine physical properties) and much lower cost of production. Among MMCs, the various conventional ex-situ processes of fabricating MMCs possess some inherent defects, such as residual microporosity, uneven distribution of reinforcement, non-wetting of the reinforcement, control of matrix-reinforcement interface, scaling up of the process for industrial utilization and processing cost. Whereas, an in-situ process produces the thermodynamically stable systems based on the in situ nucleation and growth of the reinforcements from the parent matrix. The simple technical process and optimized interface of the in-situ MMCs have attracted considerable attention recently.\(^1\)

Combustion synthesis utilizes the propagation of a combustion front through the sample to achieve material processing.\(^2\)\(^-\)\(^6\) The energy for propagation of the combustion front is obtained from the exothermic heat of the synthesis reaction. The unreacted portion in front of the combustion front is heated by this energy release, and then again undergoes exothermic synthesis.\(^2\) Combustion synthesis is a simple route for fabricating in situ composites.

Ti–Si system can form a series of intermetallic compounds, Ti\(_5\)Si\(_3\), Ti\(_3\)Si, Ti\(_5\)Si\(_4\), TiSi and TiSi\(_2\), according to Ti–Si binary alloys phase diagram as indicated in Fig. 1.\(^7\)

Among them, Ti\(_5\)Si\(_3\) is the most stable with high melting and fusing enthalpy of 2403 K and –579 KJ/mol, respectively. It has been extensively investigated as a potential reinforcement for MMCs because of the high melting point, low density, high hardness as well as good strength at elevated temperatures.\(^8\)\(^,\)\(^9\) Recently, a few works have been carried out to synthesize Ti\(_5\)Si\(_3\) through combustion synthesis reaction between Ti and Si powders with an ignition temperature of 1600 K.\(^8\)\(^,\)\(^10\) However, the high ignition temperature on the formation of TiSi compounds restricts its application for modern industry as a TiSi MMC. Therefore, it is necessary to find a simple way to fabricate TiSi MMCs at a relative low temperature. The addition of low melting metallic powder is a usually method in combustion synthesis system for reduce ignition temperature. Consequently,
the TiSi MMCs can be fabricated at a relative low temperature.

In the previous work of our group, a local in situ AlTiSi reinforced aluminium composite was successfully synthesized by SHS-cast process with reaction system of Al–Ti–Si. The purpose of this study is to develop a simplified route to produce a high quality TiSi particle reinforced steel MMCs.

2. Thermodynamic Consideration

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

\[
\frac{2}{3} \text{Ti} + \frac{1}{3} \text{Cu} = \frac{1}{3} \text{Ti}_{2}\text{Cu} \quad \Delta G^\theta_1 \quad \text{........}(1)
\]

\[
\frac{1}{2} \text{Ti} + \frac{1}{2} \text{Cu} = \frac{1}{2} \text{TiCu} \quad \Delta G^\theta_2 \quad \text{........}(2)
\]

\[
\frac{3}{7} \text{Ti} + \frac{4}{7} \text{Cu} = \frac{1}{7} \text{Ti}_{3}\text{Cu}_{4} \quad \Delta G^\theta_3 \quad \text{........}(3)
\]

\[
\frac{1}{5} \text{Ti} + \frac{4}{5} \text{Cu} = \frac{1}{5} \text{TiCu}_{4} \quad \Delta G^\theta_4 \quad \text{........}(4)
\]

\[
\frac{1}{2} \text{Ti} + \frac{1}{2} \text{Si} = \frac{1}{2} \text{TiSi} \quad \Delta G^\theta_5 \quad \text{........}(5)
\]

\[
\frac{1}{3} \text{Ti} + \frac{2}{3} \text{Si} = \frac{1}{3} \text{TiSi}_{2} \quad \Delta G^\theta_6 \quad \text{........}(6)
\]

\[
\frac{5}{8} \text{Ti} + \frac{3}{8} \text{Si} = \frac{1}{8} \text{Ti}_{5}\text{Si}_{3} \quad \Delta G^\theta_7 \quad \text{........}(7)
\]

The Gibbs free energy, \(\Delta G^\theta\) of reactions (1)–(7) has been calculated using the thermodynamic data from literature\(^{12,13}\) and their results are shown in Fig. 2. Note that the overall 1 mol of the reactants was used for the calculation of changes in the Gibbs free energy, \(\Delta G^\theta\) and the adiabatic temperature, \(T_{ad}\) in order to compare the feasibility and tendency of these reactions. It can be seen that the \(\Delta G^\theta\) of these reactions are all negative, which indicates that the seven reactions can take place. The \(\Delta G^\theta\) of reactions (5)–(7) are less than those of reactions of (1)–(4), which indicates that reactions (5)–(7) are most likely to occur. Accordingly, it can be concluded that the displacement reaction (8) can occur, i.e. \(\Delta G^\theta_8<0\), as follows.

\[
\text{Ti}_{2}\text{Cu}_{3} + \text{Si} \rightarrow \text{Ti}_{5}\text{Si}_{3} + \text{Cu} \quad \Delta G^\theta_8 \quad \text{........}(8)
\]

In order to confirm whether or not the combustion reactions can self-sustain, the critical value of copper content can be estimated by calculation of adiabatic temperature \(T_{ad}\). It is well known, in a combustion synthesis reaction process, the possible maximum temperature of an exothermic reaction can attain under adiabatic conditions. This maximum temperature is adiabatic temperature \(T_{ad}\), which can be calculated from the heat capacities and enthalpies of formation and transformation.\(^{15}\) Usually, \(T_{ad}\) can be used to ascertain whether or not a synthesis for a given material can be accomplished by a combustion synthesis method. It has been empirically suggested that combustion will not become self-sustaining unless \(T_{ad} \leq 1800\) K.\(^{15}\) The adiabatic temperature of Cu–Ti–Si system can be calculated using the following equation\(^{16}\) according to reaction (10).

\[
\Delta H_{298} + \int_{298}^{T_{ad}} \sum n_j C_p(P_j) dT + \sum n_j L(P_j) = 0 \quad \text{(9)}
\]

\[
x\text{Cu} + \frac{5(1-x)}{8} \text{Ti} + \frac{3(1-x)}{8} \text{Si} = x\text{Cu} + \frac{1-x}{8} \text{Ti}_{5}\text{Si}_{3}
\]

\[
\sum \text{..............}(10)
\]

Where \(\Delta H_{298}\) is the reaction enthalpy at 298 K, \(C_p(P_j)\) and \(L(P_j)\) are the specific heat capacity and latent heat of products, \(P_j\), \(n_j\) and \(x\) refer to the products, the mole fractions of Cu, respectively. The calculational result of Cu–Ti–Si system is shown in Fig. 3. It shows that the critical value of copper content is 43.4 wt%. When the copper content exceeds the value, the combustion reaction of Cu–Ti–Si cannot self-sustain. Therefore, in the present work the value of \(T_{ad}\) is 2261 K corresponding to the copper content of 19.04 wt%.
3. Experimental Procedure

The starting materials in this work were made from commercial powders of Cu (99.0+% purity, ~53 mm), Ti (99.5% purity, ~74 mm), Si (90% purity, ~124 mm), and 45# steel of China (composition: C 0.45, Si 0.22, Mn 0.63, Cr <0.2, Ni <0.30, Cu <0.25, P <0.035, S <0.035, Fe Bal.). Copper, titanium and silicon powder was used in the weight ratio of 10:7:4 (19.04 wt% Cu). Powder blends were dry-mixed for 8 h in a cylindrical stainless steel jar by mechanical rotation at 50 rpm, and then were uniaxially pressed into cylindrical compacts with sizes of 22 mm diameter and 5 mm height under pressures of 80 MPa. After being dried in an oven at about 120°C for 2 h to remove any trace of moisture, the compacts were placed at the bottom of a special sand mold, as shown in Fig. 4[6]. During the compaction and drying process, the powders were wrapped by aluminum foil, preventing contact of oxygen and powders. Subsequently, the steel melt prepared in a 5 kg medium-frequency induction furnace was poured into the sand mould to ignite the combustion synthesis reactions. After solidification, the local reinforced steel MMCs were formed.

Metallographic specimens were polished through standard procedure and examined using optical microscopy to observe the features of the TiSi and TiC phase in the composites. A 4% nital (CH₃CH₂OH +4 mol% HNO₃) was used as the etchant of polishing samples. The microstructures of the etched specimens were examined with scanning electron microscopy (SEM) (JSM-5310, Japan), energy-dispersive spectroscopy (EDS) (Link-Isis, Britain) and X-ray diffraction (XRD) (D/Max 2500PC Rigaku, Japan). In addition, the combustion synthesis reaction temperatures were studied by different thermal analysis (DTA) (Rigaku-8150).

4. Results and Discussion

4.1. Different Thermal Analysis Experiments

In order to study the reaction temperature of Cu–Ti–Si system, 40 mg mixtures with weight ratios of 0:20:7 and 6.7:20:7 (Cu:Ti:Si) were heated at 30°C/min to 1200°C under argon atmosphere in the DTA apparatus. The DTA curve is shown in Fig. 5, and corresponding XRD pattern is indicated in Fig. 6. It indicates that neither exothermic nor endothermic peak presents in the curve (a), mixtures with weight ratios of 0:20:7. XRD result shows that the products are Ti, Si and slight amount TiSi₂ and Ti₅Si₃ in Fig. 6(a). However, four exothermic peaks appear at temperatures of 821, 878, 971 and 1011°C in 6.7:20:7 mixtures DTA curve, curve (b) in Fig. 5. Binary Cu–Ti system is a complex system in which several different compounds exist according to phase diagram.[16] The first three exothermic peaks correspond to the TiCu formation based on Cu–Ti DTA and XRD curves in previous studies,[13] and the last peak at 1011°C corresponds to the formation of TiSi compounds. The corresponding XRD pattern shows that the reaction products are mainly as Ti₅Si₃ and a little residual Si and Ti–Cu compounds. It suggests that without Cu addition, Ti and Si do not take place obvious exothermic reaction according to DTA curves and only produce a little TiSi compounds. So we can conclude that there only exists slight reaction between Ti and Si by slight solid diffusion during continuous heating. After addition of Cu, the reaction first occurs between Ti and Cu through solid phase, forming a serious of CuTi compounds at the temperature range of 821–970°C. With the rise of temperature, CuTi react with Si, forming TiSi compound at temperature of 1011°C according to DTA result. As indicated, the reaction
sequence could be described as follows.

(I) Ti + Cu → (II) Ti$_x$Cu$_y$ + Si → (III) Ti$_a$Si$_b$ + Cu$_d$ ...

4.2. Microstructure of Steel MMC

The microstructure of steel MMC is indicated in Fig. 7. XRD results show that the composite consists of Ti$_5$Si$_3$, TiSi, Fe, TiC and residual Cu phase, as indicated in Fig. 8. Fig. 7a and b show the characters of interface and transition region. There exists a TiC particles zone near the interface in transition region with width of ~100 μm. The morphologies of TiC particles are polygon/quadrangle, with sizes of ~7 μm, as seen in Fig. 7(a). The following two reasons can be concluded for the formation of TiC particles layer. Firstly, after the combustion synthesis reaction finished, there are little silicon remained. The residual silicon can dissolve into steel melt. Secondly, due to prolonged high temperature of steel melt, a small amount of TiSi (Ti$_5$Si$_3$, TiSi) phases dissolve into steel melt as well at the interface between reinforced and matrix region, which lead to the increase of the content of Ti and Si in steel melts at the interface region. It is well known that Si can impel carbon precipitation in steel melts. Therefore, the precipitation carbon reacts with Ti, forming some particles, due to the stronger bondability between Ti and C. The exact character of transition region kept away the interface is indicated in Fig. 7(b). It shows that the zone consists of Ti$_5$Si$_3$ phase mainly, and its morphology is irregular fine graininess and coarse acicular. The coarse Ti$_5$Si$_3$ phases are dissolved in transition region by high temperature steel melt, which lead to the formation of irregular fine graininess Ti$_5$Si$_3$ phases. The character of reinforced region is indicated in Fig. 7(c) and 7(d). It indicates that the morphology of Ti$_5$Si$_3$ is short fibrous mainly near the transition region in Fig. 7(c), while that morphology changes to coarse elliptic shape or den-

![Fig. 7. Microstructure of steel matrix composite of (a) interface, (b) transition region, reinforced region (c) near and (d) far away from the transition region.](image)

![Fig. 8. XRD of TiSi (Ti$_5$Si$_3$, TiSi)/TiC reinforced steel matrix composite.](image)

5. Conclusion

The in situ TiSi(Ti$_5$Si$_3$, TiSi)/TiC locally reinforced steel matrix composite was successfully fabricated via combustion synthesized of Cu–Ti–Si system. The following conclusion can be made.

1. An in situ TiSi (Ti$_5$Si$_3$, TiSi)/TiC locally reinforced steel matrix composite was successfully fabricated via combustion synthesis in melt. The composite is composed of Fe, Cu, TiSi and Ti$_5$Si$_3$ as well as TiC phases.

2. The morphologies of the Ti$_5$Si$_3$ particles are coarse acicular/irregular particles and short fibrous/coarse elliptic shape in transition and reinforced region, respectively. TiC particles lie in transition region near the interface and their morphologies are polygon/quadrangle, with sizes of ~7 μm.

3. Due to TiSi and residual Si are dissolved into the steel melts at interface of reinforced region, local carbon is compelled precipitation by Si atoms and the reaction occurs
between local precipitation carbon and Ti atoms in steel melt, forming some TiC particles in transition region near the interface.

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