Study on reaction productions and morphology of Al-Ti-C-SiC master alloy in self-propagating high temperature synthesis

Guowei Zhang, Jingwei Niu and Hong Xu

School of material science and engineering of North University of China, Taiyuan 030051, China

Email: gwzhangas@sina.com

Abstract: Al-Ti-C-SiC master alloys were prepared by self-propagating high-temperature synthesis method with the aluminum powder, titanium powder, graphite powder and nano-SiC powder. The reaction productions and morphology of Al-Ti-C-SiC master alloy were systematically investigated. The results show that with the addition of SiC nano-particles, the reaction sequence of self-propagation synthesis of Al-Ti-C alloy was changed. During the reaction, the SiC nano-particles react with the titanium powder, which leads to an increase amounts of the TiC particles. In the self-propagation products of Al-Ti-C-SiC system, the size of TiC particles decreases first and then increases with the increase of SiC nano-particles mass fraction. When the mass fraction of SiC nano-particles is 10%, the size of TiC particles becomes nanometre, which size reach 100nm-200nm. When the mass fraction of SiC nano-particles is more than 10%, SiC nano-particles can be found in the master alloy product.

1. Introduction

Al-Ti-C master alloy synthesized by self-propagating high temperature(SHS) is a grain refiner that has been recognized as promising prospect refiner in recent years. The reaction produce Al_Ti and TiC particles as the main grain refiner, which can provide heterogeneous nucleation sites to improves the nucleation rate and enhance the performance of aluminum alloys [1-3] SiC ceramic particles have become the main reinforcement particles of aluminum matrix composites(AMS) due to the high elastic modulus, high wear resistance and low thermal expansion coefficient. How to process an excellent performance alloy through mixture the SiC particles was a topic of academic. However, the most challenging task is the poor wettability between SiC particles and Al matrix surface at low and medium temperature, so it is difficult to add the SiC particles to the aluminum matrix. Although high temperature will improve the wettability of SiC and Al matrix, SiC will react with Al to generation a hard and brittle Al4C3 phase, which is harmful to the matrix [4-7].
At present, the most commonest method is the stirring casting method [8-10]. Mixing Al and SiC particles first and adding them to liquid routes by stirring. The effect of stirring facilitate the wetting conditions of the SiC particles and Al matrix, prompt the uniform distribution of SiC particles in the liquid [11,12]. However, during the stirring process, the substrate was easily contaminate and accompany with pores that accelerate the fracture rate of the material and depress the performance of the material.

This study, therefore, base on the SHS of Al-Ti-C master alloy to raise a new method that process an Al-Ti-C-SiC master alloy by adding different quality percentage SiC particles at Al-Ti-C SHS process in order to address the above questions. On the one hand, it could facilitate wettability of SiC and Al and reduce SiC particles agglomeration. On the other hand, drop the porosity during stirring casting process. This article study the synthesis products and morphology of Al-Ti-C-SiC and found that SiC particles will change the reaction sequence of the original SHS Al-Ti-C alloy and produce nano-sized TiC particles during the reaction. In addition, as the grain refiner Al-Ti-C master alloy combine with the reinforcement SiC particles and generate Al,Ti, TiC and SiC particles disperse uniformly in the matrix. As a result, it can augment the mechanical properties of AMC materials.

2. Experiment

Commercial Al powder(99.7wt.%), Ti powder(99.9wt.%), graphite powder (99.2wt%,200 μm), SiC particles (99.5wt.%,50 nm), and high-purity aluminum (99.999%) were used in the research. To prepared composites with different fraction of SiC (all compositions were in wt% unless otherwise stated). The fraction of SiC is 0%, 5%, 10%, and 15%. The fraction of Ti in the initial group is 40%, Ti:C = 6:1, and the other groups calculate the proportion of Al,Ti,C fractions according to the proportions. Composition distribution ratio in this study has been demonstrated in table 1.

| Alloy/wt.%  | Al   | Ti   | C   | SiC |
|------------|------|------|-----|-----|
| Al-40Ti-6.67C | 53.33| 40   | 6.67| 0   |
| Al-38Ti-6.34C-5SiC | 50.66| 38   | 6.34| 5   |
| Al-36Ti-6C-10SiC  | 48   | 36   | 6   | 10  |
| Al-34Ti-5.67C-15SiC | 45.33| 34   | 5.67| 15  |

In order to prepare a Al-Ti-C-SiC master: the mixed powder is dried at 80°C for 1 h. The ball milling was done using a SP-3 planetary ball mill under argon gas for 2h. The stainless balls to material weight ratio is 6:1, and the rotation rate of the vial is 200rpm. The sufficient mixed powders were pressed into a cylinder mould and pressed at 200MPa in cold isostatic press, with the size of Φ15mm ×10mm. After that, the pressed sample is ignited by a laser with a power of 1000 W and use the high purity (99.999%) argon atmosphere protected in the process. Later, the products was diluted with high-pure aluminum, the temperature was 900°C, and the mixture was stirred for 1 min at an interval.
of 10 minutes. Finally, the suspension poured into a iron mold at 710°C to obtain an Al-5Ti-C-xSiC master alloy.

The metallographic structure specimens was observed with a ZEISS-Imager microscope. Then the morphology, micro-structure and element distribution of Al-5Ti-0.83C-xSiC master alloy were investigated by SEM and EDS (Hitachi, SU-5000). The metallographic specimens were analyzed by X-ray diffraction (XRD, Rigaku D/Max-rB, Cu, Kα radiation) and differential thermal analysis of master alloy was analyzed by DSC synchronous thermal analyzer (Setaram Labsys). The temperature range was 20~1400°C, the heating rate was 5°C/min and reaction process was under argon protection atmosphere.

3. Results and discussion

3.1. Effect of SiC nano-particles on phase of Al-Ti-C

In theory, the main reactions in the Al-Ti-C system were:

\[
\text{Ti(s.)} + 3\text{Al(l.)} \rightarrow \text{Al}_3\text{Ti(s.), 1013K} \\
\text{Al}_3\text{Ti(s.)} + \text{C(s.)} \rightarrow \text{TiC(s.)} + 3\text{Al(l.), 1186K}
\]

Figure 1 shows the XRD patterns of Al-40Ti-6.67C and Al-Ti-C-xSiC samples. In the figure 1, from the different peaks it can be found that the main products of Al-40Ti-6.67C are Al_3Ti, TiC and the remained Al. The most intense peak is Al_3Ti. With the addition of SiC in the self-propagating reaction system, in the reaction product, the peak of TiC gradually increased and the peak of Al_3Ti gradually decreased. When the SiC content reached and exceeded 10%, SiC and a small amount of Si phases appeared in the self-propagating products.

Studies have shown that [13,14], at the beginning of the non-diffusion-controlled self-propagating initial stage, the reaction proceeds quickly, the temperature continuously increases and the molten aluminum reacts with Ti. Al_3Ti generated in the aluminum-enriched area and TiAl, Ti_3Al generated in the Ti-enriched area. The final reaction product is Al_3Ti owing to the exceeded Al of reaction system.

In order to study the self-propagating reaction process, five different powders: Al/Ti, Al/SiC, Al/Ti/C, Ti/SiC, and Al/Ti/SiC were subjected to thermal analysis. The experimental results are shown in figure. 2 (a~e). The endothermic peak at 662°C is caused by melting of pure aluminum, while the exothermic peak at 721°C is the reaction between aluminum and titanium to form Al_3Ti (figure 2a); An exothermic peak appears from 1023°C, which is caused by the reaction between Al and SiC (figure 2b). The reaction equation is: 4Al (l.) + 3SiC (s.) = Al_4C_3 (s.) + 33Si(s).
Figure 1. XRD patterns of Al-Ti-C and Al-Ti-C-xSiC products.
In the DSC curve of the Al / Ti / C mixed powder (figure.2c), the first, second peak shapes and temperatures are consistent with the curve of Al / Ti powder. The exothermic peak reached at 1172°C is reaction between Al₃Ti and C. The process of forming TiC and Al; The curve of Al/Ti/SiC is shown in figure.2d. The endothermic peak formed at 1389°C because of Si appeared in the reaction product. It is indicating that the reaction between Ti and SiC will generate TiC and Si; Al / Ti / SiC mixed powder as shown in figure.2e, melting of pure aluminum corresponds to 662°C, 724°C is the formation process of Al₃Ti, 1020°C is the reaction process of Al and SiC, and endothermic heat at 1309°C is the decomposition process of Al₃Ti. In the figure 2, at 1400°C not appears obvious endothermic peak, indicating that the reaction between Al and SiC is weak and Si is generated slightly. At the same time, ref[15] pointed out that the reaction between Al and SiC requires high temperature and long time, it means that it cannot be reaction complete during the self-propagating process. Increase SiC fraction will increase the adiabatic temperature in the system and the heat storage time before ignition. besides, the reaction temperature and high temperature maintenance time will increase too. When the temperature reaches 1320°C, Al₃Ti will decompose, and the free Ti will react with SiC to form Si and TiC. With the SiC fraction increase, the decomposed Al₃Ti also increase. Therefore, the entire reaction sequence and equation of the Al-Ti-C-SiC self-propagating system is:

\[
\begin{align*}
    \text{Ti(s.)} + 3\text{Al(l.)} &= \text{Al}_3\text{Ti(s.)} \\
    4\text{Al(l.)} + 3\text{SiC(s.)} &= \text{Al}_4\text{C}_3(s.) + 3\text{Si(s.)} \\
    \text{Al}_3\text{Ti(s.)} + \text{C(s.)} &= \text{TiC(s.)} + 3\text{Al(l.)} \\
    \text{Al}_3\text{Ti(s.)} &= 3\text{Al(l.)} + \text{Ti(s.)} \\
    \text{Ti(s.)} + \text{SiC(s.)} &= \text{TiC(s.)} + \text{Si(s.)}
\end{align*}
\]

3.2. **Effect of SiC nano-particles on morphology of Al-Ti-C-SiC products**

Figure 3 is a SEM image of different fraction of SiC nano-particles self-propagating products in Al-Ti-C-SiC. As demonstrated in figure 3a, the size of TiC particles without SiC is between 0.5 and 2 μm, which shows a polyhedral morphology. When the SiC fraction is 5%. As shown in figure.3b, there
is no obvious transformation of TiC particles in the product. Since the fraction of SiC is 10% (figure.3c), it can be seen that two different size of TiC particles in the product, part of which is slightly smaller than 1 μm and another is about 0.1 μm, which reaches nanometre level. Nano-sized TiC particles are mainly generated by the reaction of Ti with SiC nano-particles that act as the reaction substrate. While the SiC mass fraction reaches 15% (figure.3d), nano-sized TiC particles have become large and is well distributed. Overall TiC particle size is relatively uniform, and the particle size is maintained at about 0.5 μm.

Ref [16,17] indicated, from a thermodynamic perspective, TiC particles with a size of 1 μm will dissolve over 1307°C. At this moment, aluminum melt existed more [Ti] and [C] particles. While the decomposition temperature of TiC that particles size is smaller that 1 μm will be lower. The Ti atoms and C atoms generated by this partially decomposed TiC can attach to the undissolved TiC causing the growth of undissolved TiC. As the SiC fraction reached 15%, the TiC particles grow larger in the products (figure.3d). Figure 4 shows particle size distribution diagram of Al-Ti-C-SiC.

Figure 5(a) shows the fractographic image of Al-34Ti-5.67C-15SiC and figure 5(b) demonstrates a surface scan energy spectrum of Si element. As shown in figure.5 (a), a large number of tiny nano-sized SiC particles are distributed on the surface of TiC particles. Lots of dispersed SiC particle are also observed in the surface scan energy spectrum of the Si element in the sample (figure.5b).

Figure 3. fractographic images of self-propagated Al-Ti-C and Al-Ti-C-SiC.

(a) Al-40Ti-6.67C, (b) Al-38Ti-6.34C-5SiC
(c) Al-36Ti-6C-10SiC, (d) Al-34Ti-5.67C-15SiC
Figure 4. Particle size distribution of Al-Ti-C-SiC.

Figure 5. Fractographic image of Al-34Ti-5.67C-15SiC self-propagating products and surface scanning energy spectrum of Si element (a)SEM 10000 ×, (b) Si elemental surface scan spectrum.

Figure 6 is a SEM image of the Al-36Ti-6C-10SiC microstructure and the surface scanning energy spectrum of the elements Ti, Al and Si. Since the matrix exclude Si element, the Si element in the energy spectrum is derived from the SiC particles. Furthermore the position where the Ti element and the Al element do not overlap is TiC particles. figure.6b and figure.6d show that in the top right and bottom right corners of the selection corresponding to the position of fine TiC particles figure.6c shows that SiC is mainly concentrated between the fine TiC particles.

The experiments show that the addition of SiC nano-particles will exert a greater impact on the morphology of TiC existed in the Al-Ti-C master alloy. TiC primarily generated at lower temperature and TiC grows up during the heating process, which the ignition temperature of self-propagating...
reaction was over 1500K. Then adding amount of SiC particles, SiC reacts with free Ti decomposed from Al₃Ti, which the reaction temperature is high and the time is short. The smaller SiC particles acted as the substrate will also reduce the TiC particles size of the product. With the SiC fraction continues to increase, the adiabatic temperature of the reaction will also increase and prolong the reaction time of the process, for which will tend to generate larger-sized TiC particles at high temperatures [18].

![Figure 6. SEM image of the Al-36Ti-6C-10SiC microstructure and the surface scanning energy spectrum of the elements Ti, Al and Si.](image)

(a) Al-36Ti-6C-10SiC self-propagating SEM image and area scanning selection location, (b) Ti element surface scanning image (black), (c) Si element surface scan (white), (d) Al element surface scan (black).

3.3. **Micro-structure of Al-5Ti-0.83C-xSiC master alloy**

The three self-propagating alloy were diluted in pure aluminum into Al-5Ti-0.83C-xSiC master alloy. The theoretical master alloy composition is shown in table 2.

Figure 7 shows the metallographic micro-structure of Al-5Ti-0.83C-xSiC master alloy with different SiC fraction. The micro-structure of the Al-5Ti-0.83C master alloy shows a large number of dispersed TiC and some thin rod-shaped Al₃Ti. A large number of agglomeration and finely dispersed
TiC are found in the Al-5Ti-0.83C-0.66SiC master alloys (figure 7b). In the micro-structure of Al-5Ti-0.83C-1.39SiC master alloy (figure 7c), it can be found that lots of dispersed distribution TiC and slightly agglomerated TiC particles. The aluminides around the TiC particles basically maintain a slender short rod-like morphology and some aluminides appear to be widened and emerge step shape. The micro-structure of the Al-5Ti-0.83C-2.57SiC master alloy (figure 7d), TiC aggregate in the form of small clusters, and the aluminum-titanium phase transform into a block and multi strip stacking which obviously become wider and shorter.

Table 2. Theoretical composition of master alloy.

| Self-propagating reaction product | master alloy      |
|----------------------------------|------------------|
| Al-40Ti-6.67C                    | Al-5Ti-0.83C     |
| Al-38Ti-6.34C-5SiC               | Al-5Ti-0.83C-0.66SiC |
| Al-36Ti-6C-10SiC                 | Al-5Ti-0.83C-1.39SiC |
| Al-34Ti-5.67C-15SiC              | Al-5Ti-0.83C-2.21SiC |

Figure 7. Micro-structure of Al-Ti-C and Al-Ti-C-SiC series master alloys.
(a) Al-5Ti-0.83C, (b) Al-5Ti-0.83C-0.66SiC, (c) Al-5Ti-0.83C-1.39SiC, (d) Al-5Ti-0.83C-2.21SiC

Liu [19] et al. Studied the possibility of the formation of Ti-rich regions around carbide particles in the Al-Ti-C system by calculating the titanium equilibrium between carbides and aluminum. The thermodynamic analysis results are identical with the earlier results of Dariel [20] et al. Partial
exceeded Ti tends to TiC particle segregation. These areas are also full of Al, which indicates that aluminum-titanium compounds will generate between Ti-rich areas around TiC and the Al matrix. This aluminum-titanium compound will form an area of Ti rich with the holding time increasing of the master alloy at high temperature, which form a layer around the TiC particles cause the TiC particles grow up.

4. Conclusion

(1) In the self-propagating Al-Ti-C-SiC product, as the SiC fraction increases (≤15%), the reaction between SiC and Ti causes the TiC fraction to increase. In the reaction process, the melt temperature rises, part of the Al₃Ti decomposes, and the Al₃Ti fraction gradually decreases.

(2) The size of the TiC particles in the Al-Ti-C-SiC products undergoes a process of decreasing first and then increasing with the increase of the SiC fraction owing to the reaction between Ti and nano-sized SiC to generate fine TiC particles. When the SiC fraction reaches 10%, residual SiC appears in the self-propagating product, and SiC is mainly distributed near TiC particles.

(3) With the increase of SiC fraction in Al-Ti-C-SiC master alloys, the morphology of Al₃Ti changes from short rod-like to step-like, the amount of TiC decreases and begin to emerge agglomeration.

(4) When the SiC fraction is over 10%, it can be seen that two different size of TiC particles in the product, part of which is slightly smaller than 1 μm and another is about 0.1 μm. These nanometre TiC particles are generated by reaction with Ti and SiC that act as the reaction substrate.

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