Application of SHS process for fabrication of copper-titanium silicon carbide composite (Cu-Ti3SiC2)

A P Amosov, E I Latukhin, A M Ryabov, E R Umerov and V A Novikov
Samara State Technical University, 244 Molodogvardeyskaya Str., Samara, 443100, Russia
E-mail: egundor@yandex.ru

Abstract. The results of the study of possibility of using a simple, energy-saving powder technology, based on the process of self-propagating high-temperature synthesis (SHS) or combustion synthesis, for the single-stage preparation of Cu-Ti3SiC2 composite from relatively inexpensive powders of its constituent elements are presented. Placing the Cu powder briquette between two adjacent charge briquettes 3Ti+1,25Si+2C for the synthesis of MAX-phase of Ti3SiC2, it was possible to use a large heat effect of SHS for melting the Cu briquette and infiltration of Ti3SiC2 porous skeleton by Cu melt. For the successful realization of this process, it is necessary to ensure the required fluidity of Cu melt and wetting Ti3SiC2 through a high temperature of the melt and the alloying of the melt with silicon, as well as to ensure the delay in the transfer of the melt into pores of SHS product.

1. Introduction

Metal matrix composite of copper-titanium silicon carbide (Cu-Ti3SiC2) attracts the attention of researchers as a promising electrical material with a low coefficient of friction, good electrical conductivity and thermal conductivity, high erosion resistance, which is important for the use in sliding electrical contacts and electrodes for electrical discharge machining of materials [1, 2]. Enhanced properties of the composite are largely due to the structure and properties of Ti3SiC2, belonging to a new class of ternary compounds with a layered structure – the so-called MAX phases, which occupy, in their properties, an intermediate position between ceramic and metal materials [3]. As of now, Cu-Ti3SiC2 composite is produced by two-stage technologies: at the first stage, Ti3SiC2 is synthesized from a mixture of Ti, Si and C powders (most often by reaction sintering), and then, at the second stage, the composite is produced from a mixture of Cu and Ti3SiC2 powders by powder metallurgy methods: vacuum sintering, hot pressing, spark plasma sintering or infiltration. Obviously, such technologies are long-term, energy-consuming, require complex and expensive equipment, so the study of the possibility of using a simple, energy-saving powder technology, based on the process of self-propagating high-temperature synthesis (SHS) or combustion synthesis, for the single-stage production of Cu-Ti3SiC2 composite from relatively inexpensive powders of its constituent elements is of great interest.

The application of the SHS process to obtain Ti3SiC2 has been studied in sufficient detail [4-7]. It is shown that the formation of Ti3SiC2 in the SHS process occurs in several stages. On the first stage, particles of solid phase TiC are formed from elemental Ti and C powders, as well as molten Ti-Si is formed. In the second stage, Ti3SiC2 particles are formed from TiC particles in the Ti-Si liquid
medium. But due to the rapid cooling of SHS products, the complete conversion of TiC and Ti-Si into Ti$_3$SiC$_2$ does not have time to pass, and the final product of SHS along with Ti$_3$SiC$_2$ contains side phases: TiC, TiSi$_2$ and others. The SHS process was first used to produce a composite based on Ti$_3$SiC$_2$ in the manufacture of electric conducting coatings of resistive heating elements [8]. During the combustion of Fe-Si, Ti and C powders, a porous cake of the conducting Fe-Ti$_3$SiC$_2$ composite was synthesized, which was ground into powder and applied by means of a binder to the surface as an electric conducting coating. Results of our previous investigations on application of SHS process for fabrication of a porous skeleton of Ti$_3$SiC$_2$ and composites on its basis with simultaneous infiltration by melts of Ni, Ti or Fe are presented in papers [9, 10]. This paper presents the results of a similar study to fabricate Cu-Ti$_3$SiC$_2$ composite.

2. Materials and methods of research

The following materials were used for the study (here and further wt.%): Ti powder of PTS brand (purity 97.95%, average particle size 100 µm), Cu powder of PMS-1 brand (99.5%; 100 µm), Si powder of Kr0 brand (99.1%; 5 µm), carbon black of P-701 brand (99.7%, average particle size 70 nm, average size of agglomerates of 1 µm). To remove moisture, the initial powders were dried at a temperature of 60–70°C. Mixing the powders was carried out in a ball mill for 1 hour. To synthesize Ti$_3$SiC$_2$, the SHS charge 3Ti+1.25Si+2C with the excess of Si content (0.25Si) was used [5, 7]. This powder mixture was used to compact by unilateral pressing the charge briquettes weighing 20 g in the form of a cylinder with a diameter of 40 mm with a relative density of about 0.5. Separately, the metal briquettes were compacted from Cu powder weighing 20, 25, 30 and 35 g in a die with a diameter of 40 mm. The scheme of experiments to study the process of SHS of MAX-phase Ti$_3$SiC$_2$ and its impregnation with molten copper is presented in figure 1.

![Figure 1. Scheme of the experiment on SHS of Ti$_3$SiC$_2$ and its impregnation with Cu melt](image-url)

The experiment was carried out in an assembly of three contiguous briquettes (a copper briquette between two charge briquettes) in an air atmosphere, with the lower part of the assembly being immersed in sand. Between Cu briquette and the upper charge briquette, a thin barrier layer of graphite powder weighing 0.5 g could be placed, protecting the upper charge briquette from being impregnated with the melt of Cu briquette. Over the upper charge briquette, there was a thin layer of sand 3–5 mm, allowing to go out expanding hot gas during the burning of the briquettes. For more dense contact of briquettes and prevention of warping the reaction products, the upper briquette was pressed against the rest through a metal washer with a load of 500 g. The ignition of the charge briquettes was carried out by nichrome resistance heating coils with the help of an ignition mixture, which was the same SHS charge, but in bulk. This ignition of briquettes could be both simultaneous and with the ignition delay of the upper briquette after the ignition of the lower briquette. Due to the heat of the SHS reaction initiated in the charge briquettes and resulting in the formation of a porous Ti$_3$SiC$_2$ skeleton in these briquettes, the middle Cu briquette was heated, melted and could impregnate the porous reaction
products of the charge briquettes. After cooling, the lower and/or upper samples of Cu-Ti3SiC2 composite were obtained, or Ti3SiC2 samples and solidified Cu layer if there was no impregnation.

The phase composition of SHS products and their infiltration with Cu melt was determined by X-ray diffraction (XRD) analysis. XRD pattern were taken using ARL X’trA (“Thermo Scientific”) diffractometer. CuKα radiation was used for continuous scanning in the range of angles 2θ from 5 to 80 degrees at a speed of 2 deg/min. The microstructure was studied using Jeol JSM-6390A scanning electron microscope (SEM), the distribution of Cu and other components along the height and radius of the synthesized samples was determined by local X-ray analysis with the use of Jeol JED-2200 attachment.

3. Results and discussion

Our experience in the preparation of Me-Ti3SiC2 composites impregnated with metals Me=Ni, Ti, Fe showed that the addition of powders of these metals to the initial SHS charge for producing the MAX phase Ti3SiC2 prevents the formation of the MAX phase, reduces its amount or completely prevents its formation depending on the amount of the additive [10]. The corresponding metal matrix composites Me-Ti3SiC2 were obtained in the case of using a separate briquette compacted from the Me powder located between two SHS charge briquettes, when the impregnation with the molten metal did not prevent the formation of the MAX phase Ti3SiC2. Therefore, in this work, the experimental scheme presented in figure 1 was used with the use of a separate briquette of Cu powder.

At first, studies were carried out using Cu briquettes weighing from 20 to 35 g with simultaneous ignition of the upper and lower charge briquettes. Experiments shown that all the briquettes were melted, but the mass of Cu briquette was greater, the smaller was the mass of Cu infiltrated into the synthesized Ti3SiC2 porous samples. This can be explained by the lower temperature of Cu melt at a greater mass of Cu briquette, which leads to a decrease in Cu melt fluidity and wetting Ti3SiC2 by Cu melt. (The wetting angle between Cu and Ti3SiC2 increases from 15 to 95° when the temperature drops from 1270 to 1089°C [11].) To assess the degree of impregnation and homogeneity of the obtained composite samples, the distribution of Cu over the sample body was studied with a 25 g Cu briquette, the main part (about 2/3) of the melt of which was absorbed into the upper sample. The Cu content was determined by local X-ray analysis along the height (the vertical axes Y1 and Y2), as well as in the middle plane along the radius (the horizontal axis X), as shown in figure 2.

![Figure 2. Scheme of local X-ray analysis.](image)

Experimental data on Cu distribution over the upper sample along different axes with a step of 1 mm are presented in figure 3, where curves 1-3 are obtained using a 25 g Cu briquette and a curve 4 – using a 30 g briquette from Cu powder of 27 g with addition of Si powder of 3 g (10%). (Curve 4 will be discussed at the end of the article.) Figure 3 shows that the maximum amount of Cu is contained in the central part of the sample. The decrease in Cu content in the peripheral part of the sample can be explained by the lower temperature in this part of the sample due to cooling and a corresponding decrease in the fluidity and wettability of the melt. Cu is evenly distributed with height in the central part, and unevenly at the periphery. A similar uneven Cu distribution was observed in Cu-Ti3SiC2 composite obtained by infiltration of Cu melt into the porous Ti3SiC2 skeleton, that was associated with the heterogeneity of the composite structure [2]. In the case of our composite, the structure is also heterogeneous (figure 4).
Figure 3. Distribution of copper in the sample on axes: 1 – Y1; 2 – Y2; 3 – X, 4 – X (Cu+10%Si).

Figure 4. The microstructure of the upper sample Cu-Ti$_3$SiC$_2$: the left figure - the region without Cu infiltration, (A) – the area of Ti carbide and silicide near the pore; the right figure - the region with Cu infiltration, (A) – the area of Ti carbide and silicide.

It is seen from figure 4 that the region without Cu infiltration is almost entirely composed of typical plates of Ti$_3$SiC$_2$, and only a small area (A) of Ti carbide and silicide is near the pore. In the Cu infiltration region, a large area of destroyed Ti$_3$SiC$_2$, consisting of a mixture of Ti carbide and Ti silicide, adjoins the Cu area. The transformation of Ti$_3$SiC$_2$ into a mixture of carbide and silicide of Ti can be explained by deintercalation of Si from MAX-phase Ti$_3$SiC$_2$ and its dissolution in Cu melt [2]. From this point of view, the addition of Si to Cu powder must impede the dissolution and deintercalation of Si from Ti$_3$SiC$_2$, thereby reducing the destruction of Ti$_3$SiC$_2$ by Cu melt, as the melt is already saturated with Si. We added 10\% Si powder to Cu powder briquette (3 g Si to 27 g Cu) and performed XRD analysis of the synthesized samples of composite (figures 5 and 6).

The comparison of these XRD patterns shows that, indeed, in the case of 10\% Si addition to Cu briquette, the relative fraction of Ti$_3$SiC$_2$ phase in the resulting composite increased markedly. Along with the main phases Cu and Ti$_3$SiC$_2$, other phases (carbides and silicides) are also visible.

The second possible reason for the decrease in the amount of Ti$_3$SiC$_2$ during Cu infiltration lies in the fact that the formation of MAX phase Ti$_3$SiC$_2$ does not begin immediately during SHS, but after a few seconds after TiC formation and lasts from several seconds to several tens of seconds [4-6]. If impregnation with Cu melt will occur at the stage of the Ti$_3$SiC$_2$ phase formation, it will interrupt the process of Ti$_3$SiC$_2$ formation and will reduce the amount of Ti$_3$SiC$_2$ in the final composite. To reduce the effect of this cause, it is necessary that the Cu melt infiltration occurs after the formation of
Ti$_3$SiC$_2$ skeleton. To this end, in further experiments, the charge briquettes were ignited at different times; in doing so, the upper charge briquette was protected from Cu melt with a layer of compacted graphite powder. In this case, the role of the upper charge briquette was limited to additional heating the Cu briquette with a delay of 5-10 seconds to facilitate Cu melting and its impregnation into the lower briquette after a period, sufficient for Ti$_3$SiC$_2$ formation upon completion of combustion. But such experiments using briquettes of pure Cu powder weighing 25, 30 and 35 g did not lead to success.

All copper was melted, squeezed out of the gap between the charge briquettes and was not included in the pores of Ti$_3$SiC$_2$. After the addition of 10% Si to a 25 g Cu briquette, two similar experiments were carried out, in the first case the delay between ignition of charge briquettes was 5 seconds, in the second case 10 seconds. As a result, in the first case 10 g of copper was absorbed into the upper sample, and in the second case 8.5 g was absorbed, that is, the barrier graphite layer did not prevent the impregnation of the upper sample with Cu melt. The masses of the lower samples, not protected from Cu melt by a graphite layer, for the first and second experiments were 33 and 31 g, respectively. The general view and microstructure of the lower sample section after SHS with delay of ignition are presented in figure 7.

Figure 7 shows a clear boundary between the regions of impregnation (2) and pure Ti$_3$SiC$_2$ (1), which was not observed in previous experiments. The microstructure of these samples confirmed the presence of a clear boundary between Cu and the plates of MAX phase Ti$_3$SiC$_2$ with the absence of intermediate layers of Ti carbides and silicides, which were observed in the composite in previous experiments with simultaneous ignition of charge briquettes due to the fact that the premature appearance of Cu melt prevented the completion of the process of conversion of Ti carbides and silicides into MAX phase Ti$_3$SiC$_2$. 
Figure 7. The general view (at the left) of the lower sample after impregnation with the Cu+10%Si melt with a 10 s delay ignition: (1) the regions of absence of impregnation; (2) the region with impregnation. Microstructure of the impregnation region (at the right).

The impregnation region in figure 7 is located in the central part of the sample with the highest temperature during SHS process compared to the peripheral part of the sample. The composition of Cu-10% Si on the phase diagram of Cu-Si system corresponds to a melting point of about 820°C, which is significantly below the melting point of pure copper 1085°C. In addition, the presence of Si in Cu melt significantly improves the wetting of Ti₃SiC₂ by the melt [11]. For these two reasons, experiments with the Cu-10% Si briquette led to wetting and impregnating the Ti₃SiC₂ skeleton but with a pure Cu briquette did not lead. For the same reasons, the Cu content in the central part of sample obtained with the use of Cu-10%Si briquette and with the simultaneous ignition of charge briquettes (curve 4 in figure 3), was considerably more than in the case of Cu briquette (curve 3 in figure 3). As this took place, the Cu distribution along the X axis became less uniform, with a low Cu content in the peripheral part of the sample, which generally corresponds to the sample in figure 7.

4. Conclusion

Thus, the application of a simple, energy-saving SHS process for fabrication of a metal-ceramic composite Cu-Ti₃SiC₂ in air in one stage has been investigated. The location of Cu briquette between two adjacent charge briquettes 3Ti+1.25Si+2C with subsequent burning of these charge briquettes allowed us to synthesize the porous MAX phase Ti₃SiC₂, and simultaneously to use a large heat effect of SHS to melt the Cu briquette and impregnate the Ti₃SiC₂ porous skeleton with Cu melt. For the successful realization of this process, it is necessary to ensure the required fluidity of Cu melt and wetting Ti₃SiC₂ through a high temperature of the melt and the alloying of the melt with silicon, as well as to ensure the delay in the transfer of the melt into pores of SHS product. It should be noted that the following studies are planned in this direction using the force SHS compaction method to fabricate the Cu-Ti₃SiC₂ composite samples with large dimensions, increased density and homogeneity, in a similar manner, how it was done to fabricate the Al-Ti₂AlC composite [12].

Acknowledgements

This work was executed at financial support of RFBR under the project No. 16-08-00867.

References

[1] Ngai T L, Zheng W and Li Y 2013 Prog. Natur. Sci.: Mater. Int. 23 70
[2] Oglezneva S A, Kachenyuk M N and Ogleznev N D 2017 Russ. J. Non-Ferr. Met. 58 649
[3] Barsoum W 2000 Prog. Solid State Chem. 28 201
[4] Gochepin B, Dubois S, Gauthier V and Vrel D 2005 VIII Int. Symp. on Self-propagating High-temperature Synthesis (21-24 June, 2005, Cagliari, Italy): Book of Abstracts p 26
[5] Meng F, Liang B and Wang M 2013 Int. J. Refr. Met. Hard Mater. 41 152
[6] Konovalikhin S V, Kovalev D Y, Sytschev A E and Shchukin A S 2014 Int. J. SHS 23 216
[7] Davydov D M, Amosov A P and Latukhin E I 2015 Appl. Mech. Mater. 792 596
[8] Lepakova O K, Golobokov N N, Kotlyar V D and Maksimov Yu M 2008 Pat. 2341839 (RF)
[9] Amosov A P, Latukhin E I and Davydov D M 2015 Modern Appl. Sci. 9 17
[10] Latukhin E I, Amosov A P, Ryabov A M, Illarionov A Yu and Novikov V A 2017 SHS 2017. XIV Int. Symp. on SHS (Sept. 25-28, 2017, Tbilisi, Georgia): Book of Abstracts p 32
[11] Lu J R; Zhou Y, Zheng Y, Li H Y and Li S B 2015 Maneyonline 114 39
[12] Fedotov A F, Amosov A P and Latukhin E I 2016 Rus. J. Non-Ferr. Met. 57 33