Self-propagating high-temperature synthesis in Ti-W-C system[①]

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[Abstract] The effects of W content and preheat temperature on combustion temperature, combustion velocity and product components of self-propagating high-temperature synthesis(SHS) in Ti-W-C system were investigated. The results show that with decreasing W content and increasing preheat temperature, the combustion temperature and combustion velocity increases, the SHS reaction becomes complete and the particle size of product increases. There exist two combustion mechanisms. When Ti powder in combustion front was molten by high combustion temperature, SHS product was formed by melt-solution-precipitation mechanism. When the combustion temperature was not high enough to make Ti powder melt in combustion front, the product was formed through diffusion-solution-in-solid-state.

[Key words] self-propagating high-temperature synthesis (SHS); Ti-W-C system; combustion mechanism

1　INTRODUCTION

Self-propagating high-temperature synthesis (SHS) or combustion synthesis, was developed by Mezhanov et al in the 1960's. Compared to traditional methods, its advantages include high-purity of products, low energy requirement, rapid reaction and simplicity of process[1]. Because of all these advantages, SHS has received considerable interest and attention.

A substantial amount of work has been done on the SHS in Ti-C system. In the 1970's, TiC, used as an abrasive with particle sizes of 1~ 200 μm and a hard alloy with particle sizes of 3~ 5 μm, was produced by the SHS method in the Soviet Union[2]. The combustion mechanism in the Ti-C system has been analyzed[3~ 6], some TiC ceramics[6, 7] and metal-TiC composites such as Al/ TiC[5, 8], Ni-Al/ TiC[9], Fe/ TiC[10], Ni/ TiC[11] have been fabricated by SHS-pressing.

SHS is based on a highly exothermic reaction. It is well known that SHS requires an adiabatic temperature (the maximum temperature to which the product can be raised as a result of the exothermic reaction) higher than 1 800 K. Because of the low heat output of the reaction W+ C $\longrightarrow$ WC, it would be difficult to fabricate WC from W and C by SHS. However, in consideration of the high heat output of reaction Ti+ C $\longrightarrow$ TiC, which probably could accelerate the combustion reaction of W+ C $\longrightarrow$ WC, this paper conducted the research on SHS in Ti-W-C system.

2　EXPERIMENTAL

The purity of Ti powder used in this study was higher than 99.5%, and the diameter was about 74 μm. The average size of W powder (> 99.5%) was 3.10 μm. Graphite powder (≥99.85%) with size less than 30 μm was used as C (carbon).

The reactant powder mixtures were prepared in the correct stoichiometric proportion for the following reaction

Ti+ W+ C $\longrightarrow$ TiC+ WC/ (W, Ti) C

where Ti and W were prepared in the ratios of W to Ti and W of 0.2, 0.3, 0.4, 0.5, 0.54 respectively.

The powder mixtures were pressed into cylindrical specimen with diameter of 20 mm and height of about 20 mm. The specimen has a relative green density of approximate 50%. After preheated at various temperature (200~ 800 ℃), the specimen was ignited by a rapidly heating W coil in an argon gas with purity of 99.999%. Once ignited, the reaction among Ti, W and C propagated down the specimen in the form of a combustion wave. During the combustion process, the combustion temperature was measured with an ultra-red ray thermometer and the propagating time was measured to calculate the combustion velocity. The phase components of the milled products were identified by X-ray diffraction(XRD) analysis. The powder morphologies of the products were investigated by scanning electron microscopy (SEM) analysis.

In order to study dynamic reaction process and investigate the combustion mechanism, the combus-

tion fronts of the specimens with the ratio of W to Ti and W of 0. 4 and 0. 54 were quenched by cold Cu blocks. Because of the great thermal conductivity of Cu, the combustion front was rapidly cooled and the high temperature structure was retained.

3 RESULTS AND DISCUSSION

3. 1 SHS combustion process

  The effect of W content on combustion temperature and combustion velocity is shown in Fig. 1. It is shown that combustion temperature and combustion velocity decline as W content increases.
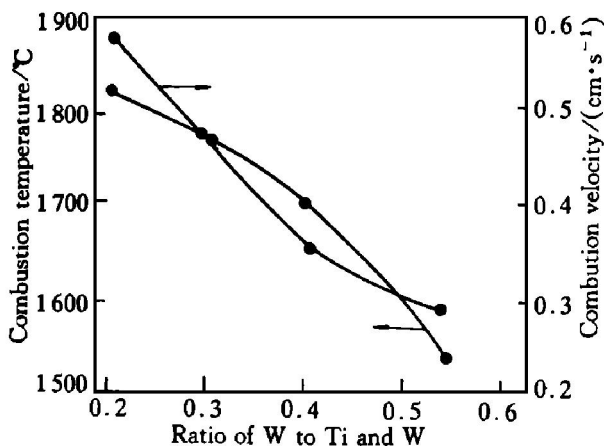

Fig. 1 Effect of W content on
combustion temperature and combustion velocity

  The effect of varying preheat temperature on the combustion process in the specimen with the ratio of W to Ti+ W of 0. 54 is shown in Fig. 2. It appears that the combustion temperature and combustion velocity are increased as the preheat temperature is raised.

3. 2 SHS products

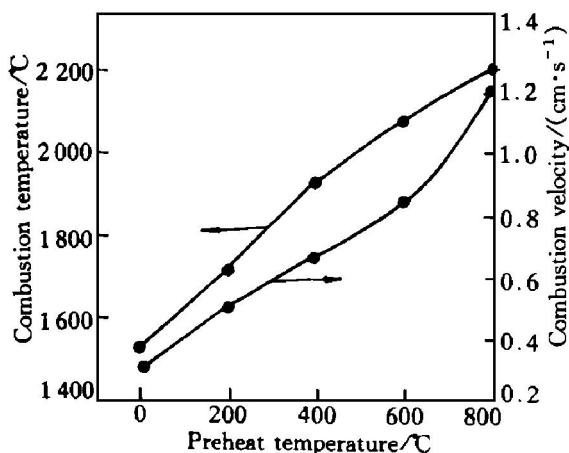 The XRD patterns of SHS products under differ-

Fig. 2 Effect of preheat temperature on combustion
temperature and combustion velocity

ent conditions are shown in Fig. 3. For the ratio of W to Ti and W of 0. 2, the product is single-phased (Ti, W) C (Fig. 3(a)). As the ratio is increased to 0. 4, the product contains mainly (Ti, W) C, there also appears a little W_2C, WC and unreacted W (Fig. 3(b)). When it is increased to 0. 54, the major phase is TiC, the amount of W_2C, WC and unreacted W is increased, and (Ti, W) C is decreased (Fig. 3(c)).

  Preheating mixtures before SHS process could accelerate the reaction and the formation of single-phased (Ti, W) C. At the ratio of W to Ti and W of 0. 4, when preheated at 400 ℃, the amount of W_2C, WC and unreacted W in products is decreased (Fig. 3(d)). When the preheat temperature is increased to 600 ℃, the product is single-phased (Ti, W) C, as shown in Fig. 3(e).

  The morphologies of milled products are shown in Fig. 4. It is seen that the particle size decreases with the increase of W content. Meanwhile, preheating mixtures before SHS process would increase the particle size.

3. 3 Combustion mechanism

  The section of the synthesized sample with the ratio of W to Ti and W of 0. 4 contains some acicular crystals, as shown in Fig. 5. These crystals indicate that at least part of the products are precipitated from a melt[12]. Fig. 6 shows the microstructure of its quenched combustion front. The energy spectrum analysis (see Fig. 7) shows that A contains Ti (79%, mass fraction, the same below) and W (21%), white spherical particle B is composed of W (78%) and Ti (22%). It is deduced that A was rapidly solidified from a liquid Ti-W melt, particle B was W which was not dissolved into liquid Ti. The black particle D is graphite. This suggests that there exists a melt-solution process during the SHS combustion of this specimen. For this specimen, the combustion temperature is 1 703 ℃ higher than the melting point of Ti, some Ti powder in the combustion front is molten, W is dissolved into liquid, Ti, C (graphite) could also be dissolved into it, then Ti-W-C melt is formed and (Ti, W) C is precipitated from the melt. This process could be described as melt-solution-precipitation mechanism. By this mechanism, because of the existence of liquid state, the grain of the product grows relatively completely.

  As the ratio of W to Ti and W is increased to 0. 54, because the combustion temperature (1 534 ℃) is lower than the melting points of Ti, the Ti powder in combustion front still remains solid, the SHS reaction among Ti, W and C would take place only through C diffusion. There were some reported data of activation energy for volume diffusion of C[13]. The activation energy for volume diffusion
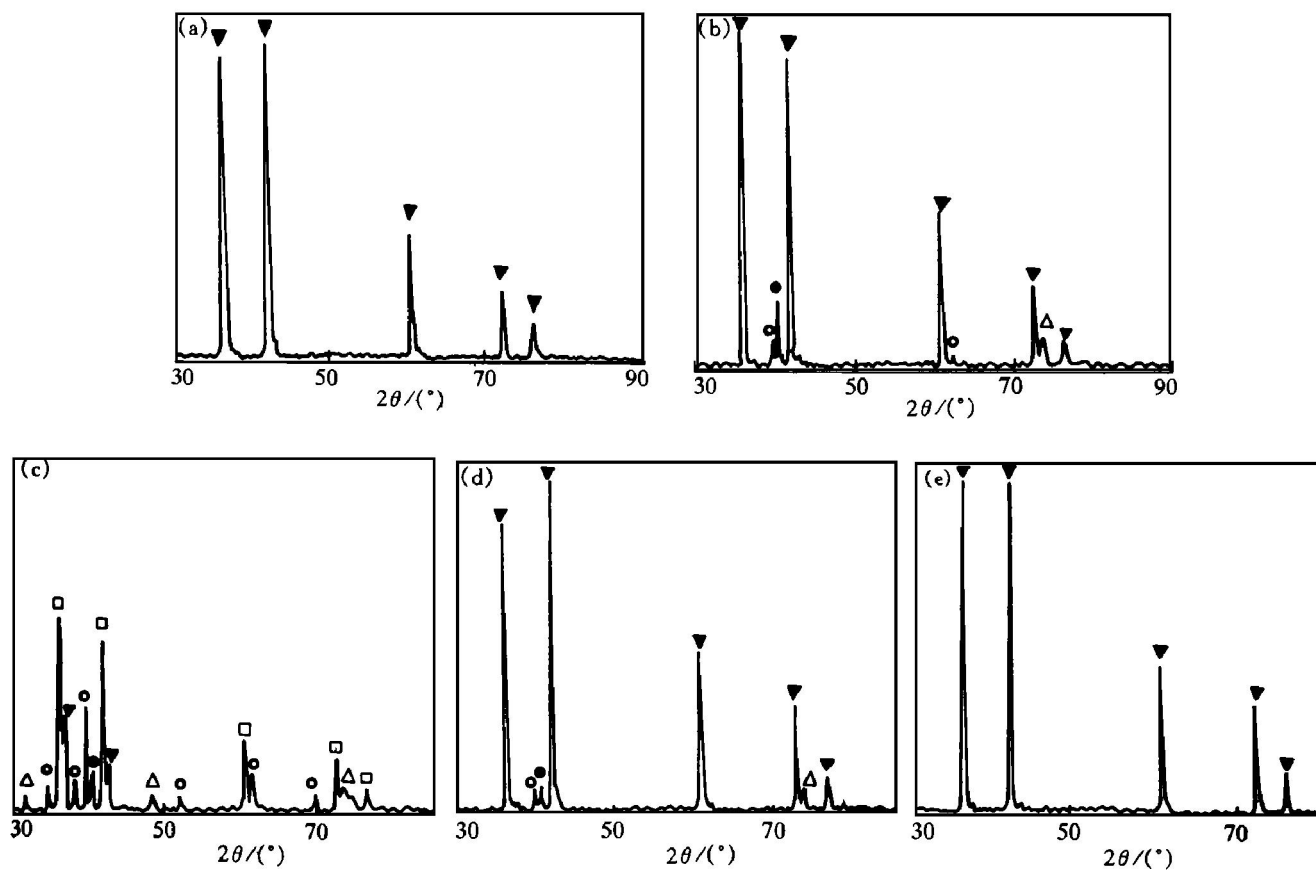
Fig. 3 XRD patterns of SHS products from specimens with different ratios of W to Ti+W
(a) —0.2; (b) —0.4; (c) —0.54; (d) —0.4, preheated at 400 ℃; (e) —0.4, preheated at 600 ℃
□ —TiC; ○ —WC; ● —W; ▼ —(Ti, W)C
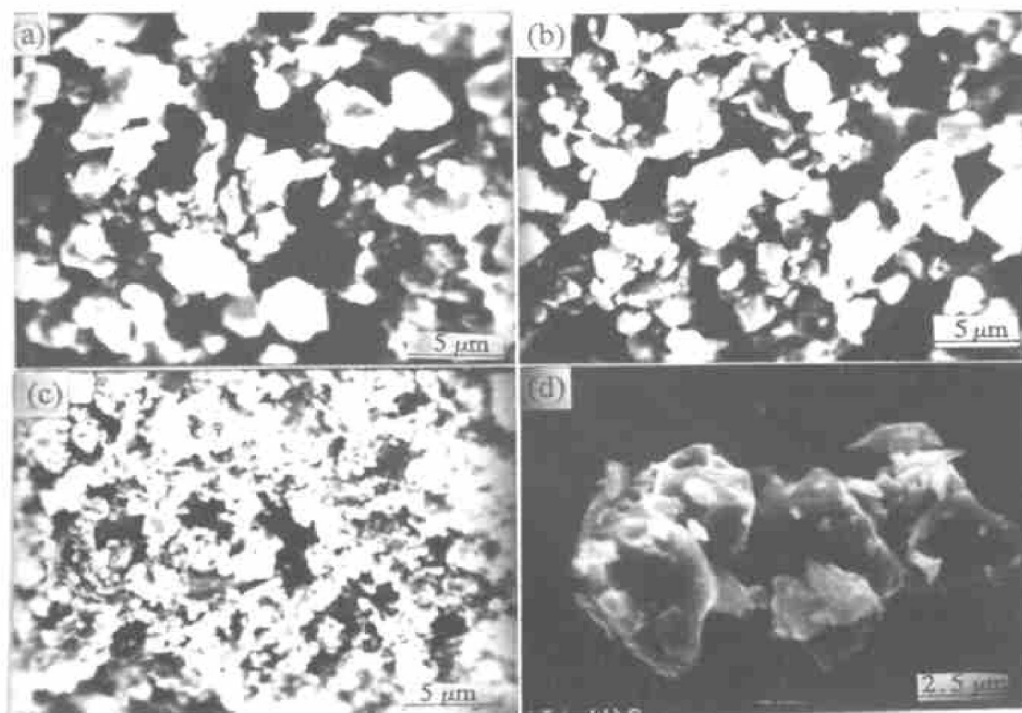
Fig. 4 SEM photographs of milled SHS products from specimens with different ratios of W to Ti and W
(a) —0.3; (b) —0.4; (c) —0.54; (d) —0.4, preheated at 600 ℃

of C in Ti is 8.4 kJ/mol, the activation energy for volume diffusion of C in $TiC_{0.97}$ is 400.26 kJ/mol, while C volume diffusion in TiC is 739.2 kJ/mol. According to the above activation energy data, That
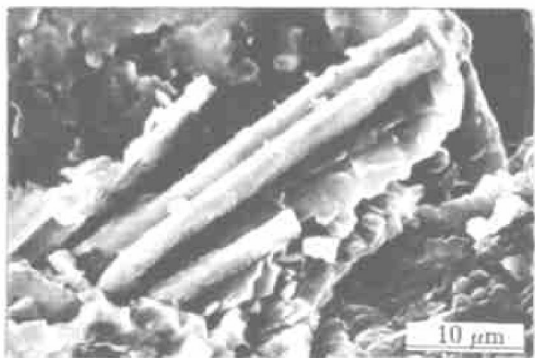
Fig. 5 Acicular crystals in synthesized
sample with ratio of W to Ti and W of 0. 4

hani et al[13] deduced that a TiC_x (x: 0~ 1. 0) layer
outside Ti powder could be rapidly formed through
the volume diffusion of C in Ti. However, after the
formation of a TiC layer, it would be very difficult for
C to react with solid Ti core to form TiC through the
volume diffusion of C in TiC, which meant that com-

pletely transformed TiC could not be formed through
volume diffusion in short SHS time. So there must be
some mechanism to accelerate the diffusion of C.

In the quenched combustion front of this speci-
men, some small cracks are found on the Ti powder
surface, as shown in Fig. 8. It is reasonable to believe
that because activation energy for surface diffusion is
much lower than activation energy for volume diffu-
sion, C could rapidly diffuse into the Ti core along the
cracks and react with Ti to form TiC. These cracks
are probably formed by thermal stress. During the
combustion process, the temperature rises rapidly at a
rate higher than 1 000 ℃/s in the combustion front.
Because of the rapid rise of the temperature, thermal
stress would be formed between different parts of sin-
gle Ti powder, which would make the Ti powder
crack.

During the reaction between Ti and C, W_2C was
formed and transformed to WC only through C diffu-
sion into W powder. Then (Ti, W)C was formed
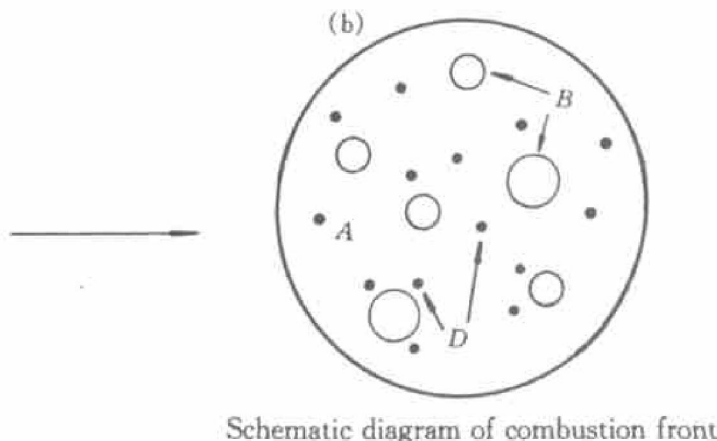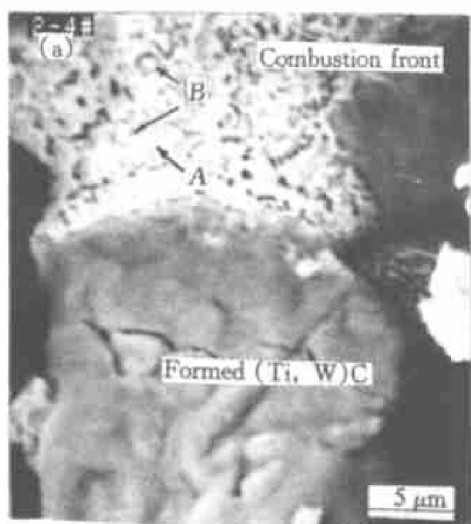
Fig. 6 Microstructure of combustion front of sample with ratio of W to Ti and W of 0. 4
(a) —Microstructure; (b) —Schematic diagram of combustion front
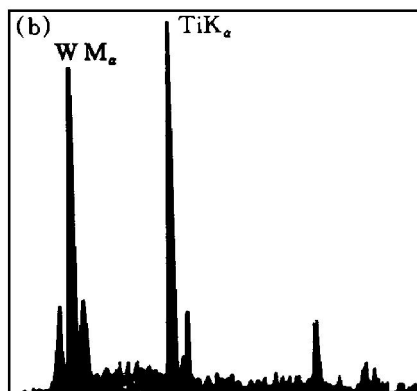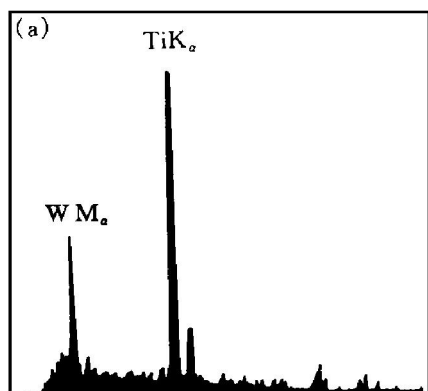
Fig. 7 Energy spectrum analysis of rapidly solidified melt A (a) and
white spherical particle B (b) in quenched combustion front of sample with ratio of W to Ti and W of 0. 4
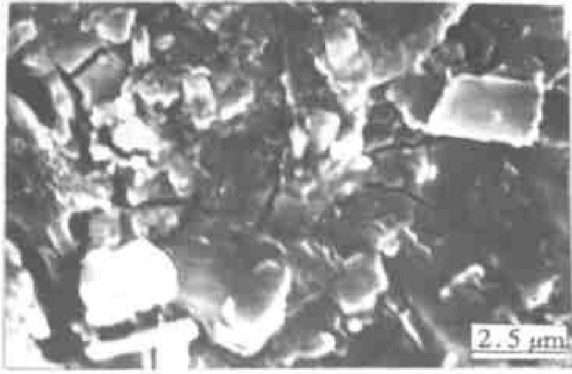
Fig. 8   Cracks on Ti powder surface in
quenched combustion front of specimen with ratio
of W to Ti and W of 0. 54

through WC solution in TiC in a solid state. Because the temperature declined rapidly after the propagation of the combustion wave, the formation of W_2C, the transformation of W_2C to WC and the solution of WC in TiC were incomplete. This combustion process could be described as diffusion-solution-in-solid-state. By this mechanism, because of the crack of the Ti powder, the product powder was small.

4   CONCLUSIONS

1) SHS process of Ti-W-C system with the ratio of W to Ti+ W less than 0. 54 could take place. Lowering W content and increasing preheat temperature would cause an increase in combustion temperature and combustion velocity.

2) The powder size of SHS product decreases with increasing W content. Preheating mixtures can improve the reaction among Ti, W and C, accelerate the formation of single-phased (Ti, W) C and increase the product powder size.

3) There exist two combustion processes. The first is described as melt-solution-precipitation; Ti powder in the combustion front is molten by high combustion temperature, W and C are dissolved into liquid Ti to form Ti-W-C and (Ti, W) C is precipitated from the melt. The second is described as diffusion-solution-in-solid-state; when combustion temperature is not high enough to make the Ti powder melt in the combustion front, cracks in Ti powder are formed during the combustion process, C diffuses along these cracks and reacts with Ti to form TiC, meanwhile W_2 C is formed and transformed to WC

through C diffusion, then WC is dissolved into TiC in a solid state to form (Ti, W) C.

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