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Effect of C particle size on the mechanism of self-propagation high-temperature synthesis in the Ni–Ti–C system

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ABSTRACT

Effect of C particle size on the mechanism of self-propagation high-temperature synthesis (SHS) in the Ni–Ti–C system was investigated. Fine C particle resulted in a traditional mechanism of dissolution-precipitation while coarse C particle made the reaction be controlled by a mechanism of the diffusion of C through the TiC_x layer. The whole process can be described: C atoms diffusing through the TiC_x layer dissolved into the Ni–Ti liquid and TiC were formed once the liquid became supersaturated. Simultaneously, the heat generated from the TiC formation made the unstable TiC_x layer break up. However, with the spread of Ti–Ni liquid, a new TiC_x layer was formed again at the interface between spreading liquid and C particle. This process cannot stop until all the C particles are consumed completely.

1. Introduction

The characteristics of extremely fast heating and high temperature in the self-propagating high-temperature synthesis (SHS) made it potential to produce materials with novel structures and properties, including ceramics, ceramic matrix composites, nanophase materials and intermetallics [1,2]. Among these materials, TiC, as a typical one of these ceramics, was paid more attention due to its low density and chemical reactivity, as well as its high hardness, good elastic modulus and high melting temperature [3].

TiC can be produced from mixtures of titanium and carbon powders by SHS. Generally, the formation of liquid and its subsequent capillary spreading are essential to the ignition and propagation of the combustion wave. However, the ignition temperature for Ti–C binary system is very high and even close to the melting point of titanium. Therefore, those second metals with low melting point are introduced to decrease the ignition temperature by forming low-melting intermetallics and evolving into a liquid at a low temperature (eutectic temperature) to improve the mass transference [4–18]. On the other hand, the fracture toughness of a TiC composite can also be improved by adding a ductile metal as a continuous phase. Among these metals, the liquid Ni form with solid TiC for the low wetting angle under vacuum at 1450 °C [19]. This makes Ni be selected as the additive metal, which can not only promote the easy occurrence of the SHS reaction, but also improve the structural applications.

However, reports on SHS reaction mechanism in the Ni–Ti–C system are very controversial. In general, the mechanism about the formation of TiC can be confirmed to be dissolution, reaction and precipitation. Nevertheless, two mechanisms about the formation of the liquid exist: one is the prior formation of Ti_2Ni formed by the solid reaction and then the formation of Ni–Ti liquid over the eutectic temperature between Ti_2Ni and Ti, which has been supported by Dunmead et al. [7], Xiao et al. [3] and Lasalvia et al. [8,9]; the other is the formation of Ti liquid caused by the direct melting of Ti during the SHS reaction, which has been suggested by Wong et al. [18]. Thus it can be seen, there is a general lack of consistency in the SHS mechanism for Ni–Ti–C system, and no firm understanding are agreed. Moreover, it is important to notice that the sizes of C particles used in the aforementioned literatures are very fine, such as carbon black and furnace black. Actually, in our previous study [20], the C particle size had a profound influence on the ignition and combustion characteristics of the SHS reaction in the 20 wt.% Ni–Ti–C system. Consequently, it can be believed to influence the SHS mechanism of the Ni–Ti–C system as well.

Therefore, the purpose of the present study is to clarify the formation mechanism of liquid and investigate the effect of C particle size on the SHS mechanism of the Ni–Ti–C system. The apparent activation energies of the SHS reactions in the Ni–Ti–C system with fine and coarse C particles are estimated to speculate the SHS mechanism by measuring the combustion temperature and wave velocity. In particular, in the Ni–Ti–C system with coarse C

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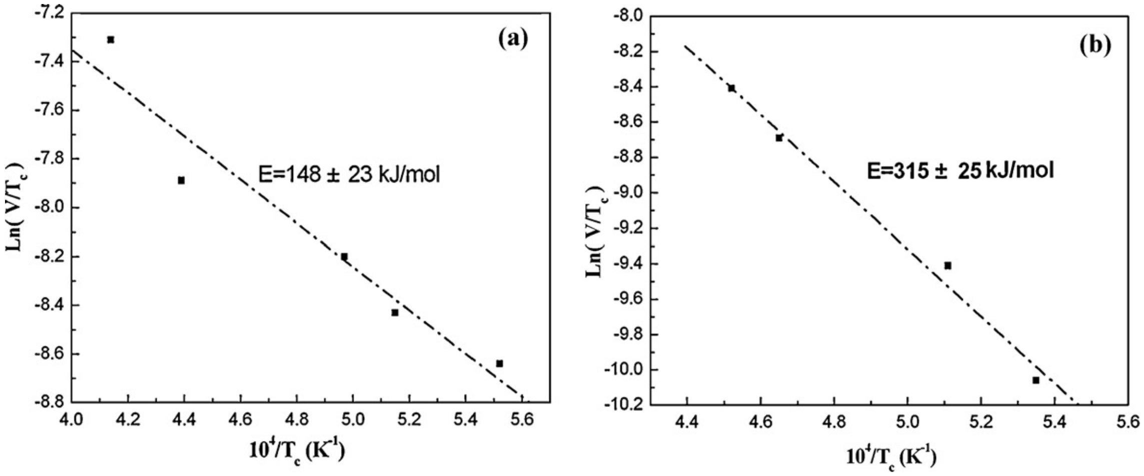

Fig. 1. Arrhenius plot of Ln(V/T_c) vs. $1/T_c$ for the SHS reaction in the Ni–Ti–C system with (a) ~1 μm and (b) ~48 μm C particles.

particle, a detailed phase transformation sequence and a delicate microstructure evolution during the passage of combustion wave are addressed to prove the speculated mechanism. It is expected that these results can be significant in effectively controlling the SHS process and promoting the use of TiC/Ni composites in practice.

2. Experimental

The starting materials were made from commercial powders of Ni (99.5% purity) with an average particle size of ~45 μm, TiC (98% purity) with an average particle size of ~48 μm, Ti (99.5% purity) with an average particle size of ~25 μm and C (99.5% purity), where two kinds of C particle sizes (with an average particle size of ~38 μm and ~1 μm, respectively) were selected.

Reactant powder mixtures were prepared for the following basic reaction:

$$\text{Ti} + \text{C} + 30\,\text{wt.\%Ni} = \text{TiC} + 30\,\text{wt.\%Ni} \tag{1}$$

The combustion temperatures were varied by controlling the addition of TiC powder which acted as an inert diluent. The reactant powders were weighed out in the proper stoichiometric proportions, keeping a constant equimolar ratio of Ti and C, but varying the amount of Ni and TiC. Three kinds of hardened steel grinding ball (1.5, 1.0 and 0.5 cm in diameter) were used as milled balls, and the amount ratio of three kinds of balls were the same. After being sufficiently dry-mixed by mechanical stirring at 25 rpm for 8 h without any liquid medium, the blends were uniaxially pressed into cylindrical preforms (20 mm diameter) under pressures to obtain green densities of 75 ± 2% theoretical density.

Details of the experimental apparatus and procedure for the SHS reaction were given in a previous article [20]. The combustion wave velocities were measured by recording the whole combustion event with a white-black CCD video camera (DALSA) at 45 frames per second. The combustion temperatures were achieved using a thermocouple pair of W–5%Re vs. W–26%Re (0.5 mm in diameter) at the centre of the perform, where the measured temperature lags 1.5 s behind the real temperature. In order to make clear the reaction sequence and phase formation mechanism in the Ni–Ti–C system with coarse C particle, the combustion wave was quenched during its passage through the sample. A long and thin rectangular sample (65 mm × 14 mm × 6 mm) favors the combustion extinguishing in the halfway by increasing heat loss and reducing heat production. In the present study, the combustion front could be made to stop by sandwiching a part of the sample between two copper plates. The quenched sample was polished and etched for phase analysis and microstructure evolution characterization. The phase constituents in the differently reacted regions were identified by the X-ray microdiffractometer (D8 Discover with GADDS, Bruker AXS, Germany) using the 800 μm beam diameter. The microstructures were investigated by using scanning electron microscopy (SEM) (Model JSM-5310, Japan) equipped with energy-dispersive spectrometer (EDS) (Model Link-ISIS, Britain).

3. Results

The propagation wave velocity and the combustion temperature can be related by Merzhanov equation [21]:

$$V^2 = \sigma_n \alpha \frac{C_p}{Q} \frac{RT_c^2}{E} k_0 \ \exp\left(\frac{-E}{RT_c}\right) \tag{2}$$

where V is the wave velocity, α is the thermal diffusivity, σ_n is a constant which depends upon the order of the reaction, T_c is the combustion temperature, and R is the gas constant, C_p and k_0 are the heat capacity and the thermal conductivity, Q is the heat of the reaction and E is the activation energy. Eq. (2) can also be expressed by:

$$2\ \text{Ln}\left(\frac{V}{T_c}\right) = \text{Ln}\left(\sigma_n \alpha \frac{C_p}{Q} \frac{R}{E} k_0\right) - \frac{E}{RT_c} \tag{3}$$

It should be noted that the thermophysical and thermochemical properties of both reactants and products are assumed to be invariable in the present calculation. Therefore, the Ln(V/T_c) exhibits a line function as $1/T_c$, and the slope is $-E/R$. The apparent activation energies of the SHS reaction can be determined from the Arrhenius plot of Ln(V/T_c) vs. $1/T_c$, and it can be calculated according to the slope. To do this, the propagation velocity and combustion temperature should be varied. This can be accomplished by adding inert phase as a diluent into the reactants. However, different starting compositions used in different experiments imply that in each experiment these parameters such as specific heat, thermal diffusivity, thermal conductivity, and most importantly, reaction heat and activation energy are different. Lakshmikantha and Sekhar [22] developed an improved kinetic equation by considering the differences of heat capacity, thermal conductivity, and density for reactants and products as well as dilution effect. The modified kinetic equation indicated that it affected only the pre-exponential factor. For the purpose of activation energies determination, the results were the same. Moreover, assuming that Ln($\sigma_n\alpha(C_p/Q)(R/E)k_0$) was a constant, we found that the Ln(V/T_c) indeed exhibited a line function as $1/T_c$, as shown in Fig. 1, which suggests that these changes caused by different starting compositions may not influence the apparent activation energies greatly. The same method as that in the present study has been widely used for activation energies determination in many literatures [7,22–25].

The combustion parameters measured in the Ni–Ti–C system with ~1 μm C particle are listed in Table 1 and are plotted in Arrhenius form in Fig. 1(a). Using the slope of the line, the apparent activation energy is determined to be 148 ± 23 kJ/mol. The combustion parameters measured in the Ni–Ti–C system with ~48 μm C particle are listed in Table 2 and are plotted in Arrhenius form in Fig. 1(b). It is worth noting that when the TiC powder with 15 wt.% was added, the SHS reaction cannot be initiated successfully. Using the slope of the line, the apparent activation energy was determined to be 315 ± 25 kJ/mol.