Synthesis of WSi$_2$ and W$_2$B intermetallic compound by in-situ self propagating high-temperature synthesis reaction

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This study is the experiments on the synthesis of Tungsten intermetallic compound (WSi$_2$, W$_2$B) by self propagating high-temperature synthesis (SHS) from two aluminothermic reactant mixture systems of WO$_3$–Si–Al and WO$_3$–B$_2$O$_3$–Al. The reactions were carried out in a SHS reactor under static argon gas at the pressure of 0.5 MPa. The standard Gibbs energy minimization method was used to calculate the equilibrium composition of the reacting species. The as-SHS products were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) with energy dispersive X-ray (EDX) technique.

Key-words : Tungsten intermetallic compound, WSi$_2$, W$_2$B, Self propagating high-temperature synthesis

1. Introduction

Tungsten (W) is an attractive material for high temperature applications because of its high melting point (3410°C). Hence, Tungsten and W-base alloys have many desirable attributes required for high temperature applications. In addition, the silicide of tungsten (WSi$_2$) and boride of tungsten based intermetallic compound (e.g. W$_2$B, WB, W$_2$B$_5$, WB$_4$ and WB$_{12}$) have a wide application as materials for modern technical use due to their unique properties such as high hardness, chemical inertness, thermal shock and corrosion resistance at high temperature, electronic conductivity, and have potentially industrial applications such as abrasive media, turbine blades, the nozzle of a gas burner, electrode materials, crucibles and ingot molds for precision metallurgy and thin film of electronic components, which are exposed to exacting environments. Furthermore, the boride of tungsten (W–B system) has been a promising reinforcement for carbon materials and refractory carbides such as B$_4$C and WC while, the silicide of tungsten are frequently considered as a second phase particularly for zirconia or carbides composite system (e.g. WSi$_2$–ZrO$_2$, WSi$_2$–MoSi$_2$–SiC).

Tungsten based intermetallic alloys are usually produced by solid state reaction between pure elements powders at high temperatures, which is carried out in multistage process. The synthesis process can be described base on mechanical mixing of elemental reactant powders followed by high temperature reaction sintering or hot isostatic pressing process (HIP). Recently, self propagating high-temperature synthesis (SHS) method has been developed to produce ceramics, intermetallics, catalysts, composite and alloys and magnetic materials at low cost. It is based on the use of highly exothermic reactions which are commonly found when synthesizing such materials. This method exploits self-sustaining solid-flame combustion, which develops very high temperatures inside the materials over a short period. A stoichiometric mixture of the reactant powders, carefully mixed, were pressed to obtain a powder compact are the common steps. The sample is then heated locally, thus reducing the heat consumption to synthesize the ceramic or alloys. As the reaction is highly exothermic, it releases a lot of heat which will, in turn, heat the inside of the sample. Where the reaction will be able to start and progressively, the reaction front will be able to propagate through the sample until the reactants are completely converted (shown in Fig. 1). SHS method therefore offers many advantages over traditional methods, such as much lower energy loss, lower environmental impact, convenient manufacturing process and unique properties of the product.

Here, we present the WSi$_2$ and W$_2$B intermetallic compound in which resulting from SHS reaction. The thermodynamic study of in-situ reactions as well as their resulted products microstructure and phase composition was investigated.

2. Experimental

2.1 Raw materials

The reactants used in this study were tungsten oxide (WO$_3$), silicon lump (Si), boron oxide (B$_2$O$_3$) and aluminum metal (Al) powders which the microstructure are viewed in Fig. 2 and their properties are listed in Table 1.
2.2 Experimental procedure

The general exothermic chemical reaction formula of as-SHS products can be express in Eqs. (1) and (2).

\[
\begin{align*}
\text{WO}_3(s) + 2\text{Si}(s) + 2\text{Al}(s) & \rightarrow \text{WSi}_2(s) + \text{Al}_2\text{O}_3(s), \quad \Delta H^{\circ}_{298K} = -909.23 \text{kJ/mol} \quad (1) \\
\text{WO}_3(s) + 0.5\text{B}_2\text{O}_3(s) + 3\text{Al}(s) & \rightarrow \text{WB}_6(s) + 1.5\text{Al}_2\text{O}_3(s), \quad \Delta H^{\circ}_{298K} = -907.71 \text{kJ/mol} \quad (2)
\end{align*}
\]

The powders were mechanical activated and dry mixed in the planetary ball milled (Tungsten carbide-cobalt jar and ball) (Fritsch GMBH, Pulverisette 6) at a rotational speed of 250 rpm for 1 h. The resulted particle size of powder mixture for the WO₃–Si–Al system was 15.6 μm and WO₃–Si–Al system was 14.8 μm. The powder mixture was uniaxially pressed (Herzog, TP20P) without binder at 30 MPa into cylindrical pellets compact of 25.4 mm diameter represented in Fig. 3. The compact were placed on a graphite plate with 15 mm diameter hole at the center. Then, the compact and graphite plate was transferred to SHS reactor and placed on a movable graphite plate. The reaction chamber was evacuated with a vacuum pressure of 70 mmHg for 5 min and filled with Argon gas up to a pressure of 0.5 MPa. This operation was repeated at least twice in order to ensure an inert environment during reaction revolution.

The experimental setup in this work schematically represented in Fig. 4. It consisted of a SHS reactor with a controlled atmospheric reaction chamber and tungsten filament connected to a power source through a current controller, which provides the energy required for the ignition of the reaction. Then, under self propagating conditions, the reaction front travels until it reaches the opposite end of the sample.

After the SHS reaction, the product was allowed to cool to room temperature and then taken out of the reactor.

2.3 Characterization

The chemical composition of the resulting products were investigated by X-ray diffraction (XRD, PHILIPS, X'Pert MPD with Cu Kα radiation, λ = 1.54 Å, Netherlands). The morphology and elemental analysis were determined by using scanning electron microscope (SEM, JSM-5800LV, JEOL, Japan) with energy dispersive X-ray spectrometer (EDX, ISIS 300, Oxford).

3. Results and discussion

3.1 SHS-product characteristic

The images of the typical SHS-product after the reaction event can be seen in digital photograph in Fig. 5. The products were separated into two immiscible phases. The heavy intermetallic compound was located at the bottom and the lighter phase of oxide ceramic slag was located on the top. These processes were controlled by surface tension and buoyancy force owing to difference density of the product.

3.2 Thermodynamic analysis

Thermite reaction (or reduction) was used in our study to produce these materials. In general, this process involves oxides...
and reducing metal. The overall scheme of thermite-like SHS reactions can be represented as follows.12)

\[(O_{x1} + O_{x2} + O_{x3} + \cdots + O_{xn}) + \text{R} \rightarrow \text{polymetallic alloy} + R_x O_y + Q\] (3)

Where, \(O_{xi}\) stands for the oxides of W, Si and B; R is metal reducer (Al), and Q is the heat of reaction.

Thermodynamic calculations were performed for equilibrium concentration of stable species produced by SHS reactions based on the Gibbs energy minimization method.13,14) The evolutions of species were calculated under reducing atmosphere condition and as a function of temperature in the temperature range of 0–3500°C. The calculation was assumed that evolved gases were ideal and formed ideal gas mixture and the condensed phases were pure. The total Gibbs energy of the system can be expressed by the following equation:

\[ G = \sum n_i (g_i^\circ + RT \ln P_i) + \sum n_i g_i^\circ + \sum n_i (g_i^\circ + RT \ln x_i) \] (4)

\[ \text{gas} \quad \text{condensed solution} \]

\[ G = \sum n_i (g_i^\circ + RT \ln P_i) + \sum n_i g_i^\circ + \sum n_i (g_i^\circ + RT \ln x_i) \] (5)

Where, \(g_i^\circ\) is the standard molar number of species i; \(P_i\) is the partial pressure of species i; \(x_i\) is the molar fraction number of species i; and \(y_i\) is the activity coefficient of species i. The exercise is to calculate \(n_i\) in a way \(G\) is a minimized subject to mass balance constraints.

The adiabatic temperature \(T_{ad}\) of the SHS process can be calculated from the enthalpy of the reaction.6) This is the maximum theoretical temperature that the reactants can reach, and it is determined from Eq. (5). This equation applies to phases change occurring between the initial temperature and \(T_{ad}\). The calculated \(T_{ad}\) of overall reaction from Eqs. (1) and (2) is 3398.7 and 3313.2°C, respectively.

\[ \Delta H = \int_{298}^{T_{ad}} C_p \text{solid} \, dT + \Delta H_f + \int_{T_{ad}}^{T_m} C_p \text{liquid} \, dT \] (5)

Where, \(\Delta H\) is the enthalpy of the reaction, \(\Delta H_f\) is the enthalpy of transformation, \(C_p\) is the specific heat capacity, \(T_{ad}\) is the melting temperature, and \(T_{ad}\) is the adiabatic temperature.

It had been accepted that, the reaction can be a self-sustained manner due to its exothermic character, when the adiabatic temperature of the reaction is higher than 1800°C.10) The calculated adiabatic temperature of the WO$_3$–Si–Al and WO$_3$–B$_2$O$_3$–Al system are higher than 1800°C, thus the using of SHS is feasible for these systems.

3.3 Synthesis of WSi$_2$ intermetallic compound

The equilibrium composition of the WO$_3$–Si–Al system at different temperatures was calculated using “HSC” computer software15) based on Gibbs energy minimization method and the results are shown in Fig. 6. The formation of WSi$_2$ was initiated at almost 2000°C, with a decrease in the amount of reactants.

During the passage of a combustion front in the SHS reaction, WO$_3$, Si and Al in the Eq. (1) may interacted to form some possible compounds as the following intermediate chemical reactions.

\[ 2\text{Al} + 3\text{WO}_3 \rightarrow 3\text{WO}_2 + \text{Al}_2\text{O}_3, \quad \Delta G = -834.82 \text{kJ/mol} \] (6)

\[ 4\text{Si} + 3\text{WO}_3 \rightarrow 3\text{SiO}_2 + \text{Al}_2\text{O}_3, \quad \Delta G = -28.08 \text{kJ/mol} \] (7)

**Figure 7** shows the theoretical calculated results of Gibbs energy of reactions versus temperature from the reaction of Eqs. (6) and (7). After ignition at the melting point of Al
(660°C), the reaction (6) took place and followed by reaction (7) to form \(\text{Al}_2\text{O}_3\) and \(\text{WSi}_2\) as solid phases and \(\text{SiO}\) as a gas phase.

Figure 8(a) shows the XRD patterns of the intermetallic product prepared from the \(\text{WO}_3\)-\(\text{Si}-\text{Al}\) mixture. All peaks indicate the presence of only the tetragonal \(\text{WSi}_2\) phase (JCPDS no. 03-065-2646). The composition in the ceramic slag from the \(\text{WO}_3\)-\(\text{Si}-\text{Al}\) mixture is shown in Fig. 8(b). As can be seen from this XRD patterns that the \(\text{Al}_2\text{O}_3\) (JCPDS no. 01-076-0144) was a major component, whereas, the \(\text{WSi}_2\) intermetallic was a minor residual phase.

The SEM image in Fig. 9 shows the overall formation of \(\text{WSi}_2\) microstructure. It is clearly seen as a cracking surface of continuous intermetallic matrix phase. Phases confirmation was performed by the EDX spectrum as viewed in Fig. 10.

### 3.4 Synthesis of \(\text{W}_2\text{B}\) intermetallic compound

The equilibrium composition of the \(\text{WO}_3\)-\(\text{B}_2\text{O}_3\)-\(\text{Al}\) system at different temperatures was calculated using HSC\textsuperscript{TM} computer program based on Gibbs energy minimization method and the results are shown in Fig. 11. The formation of \(\text{W}_2\text{B}\) is initiates approximately at 1000°C.

During the process of SHS, \(\text{WO}_3\), \(\text{B}_2\text{O}_3\) and \(\text{Al}\) in the Eq. (2) may interacted to form some possible compounds as the following intermediate chemical reactions.

\[
2\text{Al}(l) + 3\text{WO}_3(s) \rightarrow 3\text{WO}_2(\alpha) + \text{Al}_2\text{O}_3(\alpha), \quad \Delta G = -199.52 \text{ kJ/mol} \tag{8}
\]
Figure 12 shows the Gibbs energy of the reaction of Eqs. (8)–(11), respectively. As well as, for the WO$_3$–B$_2$O$_3$–Al system, the reaction was completed and produced the final products if the reactants were located in the same area or has suitable of the reaction steps. The reactions began at the melting point of Al reacts with metal oxide of WO$_3$ to form intermediate phases of WO$_2$ [Eq. (8)]. Then, these intermediate phases reacted with the residual molten Al together with B$_2$O$_3$ and yield metal element of W, B and Al$_2$O$_3$ [Eqs. (9) and (10)]. Later, the heat releases from the previous reactions was then help formed W–B binary phase of W$_2$B product [Eq. (11)].

Figure 13(a) shows the XRD patterns of the intermetallic product prepared from the WO$_3$–B$_2$O$_3$–Al mixture. Major peaks indicate the presence of the tetragonal W$_2$B phase (JCPDS no. 01-073-1767). In addition, these intermetallic regions still slightly contained with W–Al intermediate phase and pure W. The W–Al intermediate phase was formed from the rapid cooling down and solidification of the reaction. The composition in the ceramic slag from the WO$_3$–B$_2$O$_3$–Al mixture shows in Fig. 13(b). As can be seen the Al$_2$O$_3$ (JCPDS no. 01-076-0144) is a major component, whereas, the W$_2$B intermetallic and W element were minor residual phases.

The microstructure of product from the WO$_3$–B$_2$O$_3$–Al system was shown in Fig. 14. As can be seen the typical W$_2$B intermetallic is nucleated into a large rod-like crystals. The EDX spectrum in Fig. 15 shows tungsten and boron elements as a rod-like matrix phase, therefore, the W–B binary compound or W$_2$B stable phase was expected.

4. Conclusions

The results reveal that the self-propagating high-temperature synthesis (SHS) method can be used to produce WSi$_2$ and W$_2$B intermetallic compound from the reactants system of WO$_3$–Si–Al.
and WO$_3$–B$_2$O$_3$–Al with the benefits of energy saving and minimization of production time.

The purity and dense of WSi$_2$ and W$_2$B intermetallic compound materials obtained by this method may be further improved by self-propagating high-temperature synthesis-casting (SHS-casting) process.

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