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Effect of diluent on the synthesis of molybdenum disilicide by mechanically-induced self-propagating reaction

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ABSTRACT

The effect of the addition of diluent to Mo–Si system on the formation of $MoSi_2$ by mechanically-induced self-propagating reaction was investigated in a high-energy ball mill. $MoSi_2$ intermetallic was added as diluent to Mo–Si powder mixture. The structure and morphology of the reaction product was analyzed by X-ray diffraction and scanning electron microscope. The diluent decreased the adiabatic temperature, increased the ignition temperature and modified the Mo/Si reactants interface. Therefore, the incubation period of mechanically-induced self-propagating reaction was extended from 90 min to 140 min with the addition of diluent from 0 wt% to 10 wt% to Mo–Si powder mixture. The extended milling time reduced the size of agglomerated particles and fine $MoSi_2$ product was obtained.

1. Introduction

Molybdenum disilicide ($MoSi_2$) is currently of great interest as potential high-temperature structural materials because of its excellent stability in oxidation and corrosive environments. It is difficult to synthesize pure $MoSi_2$ by conventional casting and powder pressing/sintering methods due to its high melting point (2030 °C) and narrow compositional range [1]. The synthesis of $MoSi_2$ by self-propagating high-temperature synthesis (SHS) and mechanical alloying (MA) have been shown in numerous investigations [2–6]. Self-propagating high-temperature synthesis (SHS) is a chemical reaction in a certain atmosphere to ignite powder compacts. The process is highly exothermic. The exothermic reactions is initiated at an ignition temperature T_{ig}, and generates heat which is manifested in a maximum or combustion temperature, T_c (e.g. 1000–6500 K), which can volatilize low boiling point impurities, and results in purer products than those produced by conventional techniques [7]. SHS has engaged considerable attention as an affordable process to prepare a variety of refractory and high-temperature materials. These have been demonstrated in numerous investigations [7,8]. However, it is difficult to control the processing parameters of combustion synthesis reaction, and the end-product is largely porous powder compact.

Mechanical alloying (MA) is a solid-state powder processing technique. It involves repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill [9]. MA is capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or pre-alloyed powders [6,9]. The synthesis of a variety of alloy phases including solid solutions, quasicrystalline and crystalline intermetallic phases, and amorphous phases has spurred lots of research investigations in recent years [9,10]. However, the MA time is large to obtain the end products, sometime hundreds of hours [6,10] and is not suitable for industrial production.

It is well known that when a highly exothermic chemical system is mechanically treated by ball milling, a combustion-like reaction can take place. This process is generally referred as mechanically-induced self-propagating reaction (MSR) [11–13]. This process combines the advantages of SHS and MA techniques. The end-product is pulverized into fine particles. The milling time of MSR is short [11–14] and reduces the contamination from the balls and vials. Several researchers have reported the (explosive) formation of $MoSi_2$ during mechanical alloying by mechanically-induced self-propagating reaction [11,14].

The addition of diluents to the reactants will affect the milling process and the properties of the end-product will change. Jo et al. have reported the effect of the diluent content on $MoSi_2$ synthesized by self-propagating high-temperature synthesis [2]. However, it is difficult to find any research report on the effect of the diluent on the formation of $MoSi_2$ by mechanical alloying. The objective of this study is to investigate the effect of the

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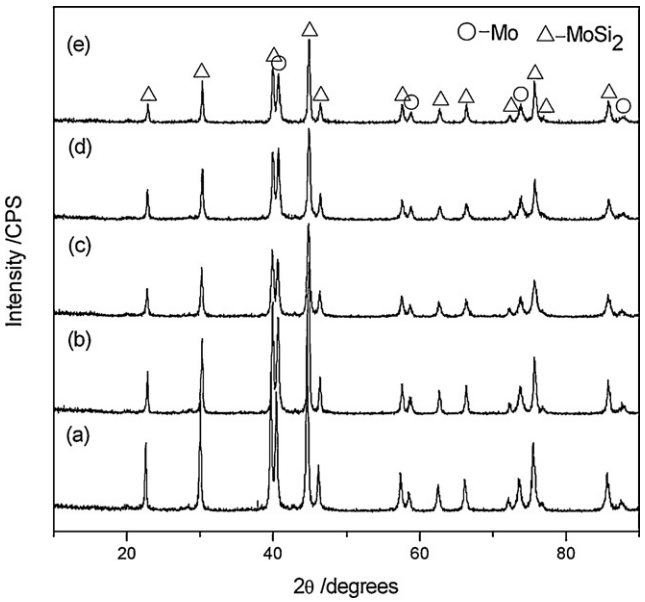

Fig. 1. The X-ray diffraction patterns taken at the induction time of mechanically-induced self-propagating reaction with various $MoSi_2$ diluent content (a) as-milled for 90 min powder without diluent; (b) as-milled for 100 min powder with 2.5 wt% diluent; (c) as-milled for 110 min powder with 5.0 wt% diluent; (d) as-milled for 120 min powder with 7.5 wt% diluent; (e) as-milled for 140 min powder with 10.0 wt% diluent.

diluent content on the behavior of mechanically-induced self-propagating reaction of Mo–Si system during mechanical alloying process. Based on the experimental results, a new method to alter the incubation time of MSR is proposed. Modification of incubation time will control the particle size of the final product. The structure and morphologies of MSR powders are discussed by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively, according to the proposed method. A fine grain structured product is obtained by the addition of diluent.

2. Experimental procedures

The starting materials used in the present study were 99.9% pure elemental molybdenum powder with an average particle size of 3–5 μm and 99.9% pure elemental silicon powder with an average particle size of 44 μm. The mixture of elemental powders was prepared with the molar ratio of molybdenum to silicon being equal to 1:2. And then the diluent, $MoSi_2$ intermetallic powder, was added into the mixture of molybdenum and silicon. The content of the diluent was 0 wt% ($0^{\#}$), 2.5 wt% ($1^{\#}$), 5.0 wt% ($2^{\#}$), 7.5 wt% ($3^{\#}$), 10.0 wt% ($4^{\#}$), respectively. The mechanical alloying was performed using a high-energy vibratory ball mill. Three stainless steel vials (60 cm^3 in volume) with bearing steel balls (10 mm and 6 mm in diameter) were used for milling. The frequency of vibration of the machine was 1000 rev min^{-1}.

For each milling run, 5.0 g of the powder mixture was canned into the stainless steel vials containing bearing steel balls in a glove box container under an argon gas atmosphere to avoid contamination from air. The weight ratio of the balls to the powder mixture was 15:1. The vials were sealed with a rubber O ring and the milling thus proceeded in a stationary argon atmosphere. The milling program was set to pause for 6 min for every 10 min of milling to prevent excessive heating during the milling process. The surface temperature on the top of the vial was measured with a digital thermometer at intervals. When an obvious abrupt temperature increase was observed [15], the milling time was suggested to be the critical ball milling time (incubation period) of self-propagating reaction during mechanical alloying.

The structure of milled powders was analyzed by a Rigaku D/max-RB X-ray diffractometer using Cu target ($K\alpha$, $\lambda = 0.15406$ nm) operating at 40 kV and 200 mA settings. The morphologies of milled powders were investigated using a Kevex LEO-1450 scanning electron microscope (SEM).

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of samples with different diluent content after different milling times. The milling time represents the time for the occurrence of mechanically-induced self-propagating reaction (MSR) during mechanical alloying. At this particular time, the surface temperature of the vial shows an acute variation. The strong peaks are of $MoSi_2$ in all samples (Fig. 1). $MoSi_2$ is synthesized by mechanically-induced self-propagating reaction after incubation period. In the present study, not all the Mo and Si powder mixture took part in the mechanically-induced self-propagating reaction (MSR). And some Mo(Si) solid solution was residual (the site of Mo peaks in Fig. 1). In other words, the MSR in the present process was not uniform or integral. This is due to relatively low adiabatic temperature of $MoSi_2$ (1942 K), which only is 143 K higher than the experiential suggestion of SHS (1800 K) [7]. The adiabatic temperature (T_{ad}) is the maximum combustion temperature of self-propagating high-temperature synthesis reaction under adiabatic conditions. It is calculated from the enthalpies of formation and specific heat of the product. On the basis of experimental observations, it has been suggested that systems with $T_{ad} \leq 1800$ K will not react in a self-propagating manner [7,8]. The powder is loose during mechanical alloying process, and the loose powder exhibits the state of the poor particle-particle contacts in the vial [16]. Therefore, the exothermic reaction ignites locally at one point. And, it is difficult that the heat evolved during the exothermic reaction propagates and ignites the reaction in other regions of reactants. Additionally, a part of heat is consumed in increasing the temperature of vial and balls. When the heat is not sufficient for SHS, the self-propagating reaction will extinguish. Simultaneously, the combustion wave is propagating irregular, in some instances, the wave propagates down at an angle. This is supported by the presence of strong Mo diffraction peaks (Fig. 1) and confirms the presence of residual reactants. These residual reactants transform into compound during subsequent heat treatment at relatively low temperature, such as at 700 °C in vacuum [17]. It can also be seen from Fig. 1 that the incubation period of mechanically-induced self-propagating reaction (MSR) is prolonged from 90 min to 140 min with the increase of diluent. This indicates that the energy inducing the MSR is increased with the diluent content. This is well in accord with the previous findings where excessive Si acted as diluent and extended the incubation time and increased the ignition temperature of the powder mixture [18,19].

The grain size, strain and lattice parameters of Mo and $MoSi_2$ are calculated from X-ray diffraction measurements, and they are shown in Tables 1 and 2, respectively. Table 1 shows that the grain size of Mo is decreasing with milling time. The stress induced due to mechanical alloying is conventionally described in terms of strain.

Table 1
Grain size, strain and lattice parameters of Mo.

Sample no.	Grain size (nm)	Strain (%)	Lattice parameters (nm)		
			a	*b*	*c*
0	26.4	0.3803	0.31524		
1	25.2	0.3957	0.31416		
2	22.1	0.4500	0.31437		
3	20.8	0.4805	0.31463		
4	19.2	0.5251	0.31409		

Table 2
Grain size, strain and lattice parameters of $MoSi_2$.

Sample no.	Grain size (nm)	Strain (%)	Lattice parameters (nm)		
			a	*b*	*c*
0	47.7	0.2222	0.32088		0.78574
1	41.1	0.2089	0.31999		0.78367
2	39.0	0.2458	0.31989		0.78374
3	38.7	0.2541	0.31990		0.78192
4	36.4	0.2357	0.32012		0.78273