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Synthesis of pure molybdenum disilicide by the "chemical oven" self-propagating combustion method

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Abstract

A high pure molybdenum disilicide was prepared by using the "chemical oven" enhanced self-propagating combustion method. The mixtures of Si and Ti were ignited as chemical oven. Ammonium chloride was added to the mixed powders to control the propagation rate of combustion. The compostion of product was detected by X-ray diffraction (XRD) and X-fluorescence analysis. Results show the molybdenum disilicide product is single phase with trace impurities. Scanning electron microscopy (SEM) photos show the product by chemical oven self-propating high temperature synthesis (SHS) method is more homogeneous than the product by normal SHS method.

Keywords: A. Powders: solid state reaction; D. Silicides; Chemical oven

1. Introduction

$MoSi_2$ (molybdenum disilicide) has attracted great research interest due to its rather low density (6.31g/cm^3), high melting point, high electrical conductivity and very good oxidation resistance at high temperature, even in very aggressive environments [1–9]. It is useful in such applications as high temperature heating elements and possible structural parts at elevated temperature. Industrially, $MoSi_2$ is produced by reaction of Mo and Si powder mixtures at relatively low temperatures (typically 1200–1400 °C for 2–4 h). The product of such a reaction is in the form of hard sintered compacts that are broken up and milled to produce powders of $MoSi_2$ for subsequent processing.

Combustion synthesis, or self-propagating high temperature synthesis (SHS) is a technique for producing ceramics, intermetallic, and composite materials. The utilization of the SHS process for the preparation of $MoSi_2$ powder has been reported by various researchers [10–13]. In this paper we introduce a novel process called chemical oven SHS (COSHS) to obtain high pure single-phase $MoSi_2$ powder. In the COSHS mode of combustion, the reactant pellet outside is ignited at upper surface by a high-energy heat input and layerwise combustion occurs at a definite rate of wave propagation. The reactant pellet inside is warmed up by the heat given out from the reaction outside and then ignited at the bottom surface contacted with the reactant outside. Because of the increased reaction temperature and long-time at high temperature, the reaction between Mo and Si is carried out thoroughly and impurities are evaporated completely.

2. Experiment

The materials used in this study were 98.5% pure Mo powder with a particle size range 2–5 μm and 99.4% pure Si powder with an average size of 10 μm . NH_4Cl (99.9 wt.%) as an additive was added to some samples for the fabrication of pure $MoSi_2$ intermetallic. The samples were prepared according to the composition shown in Table 1.The mixtures were ball-milled for 24 h using Si_3N_4 balls. Absolute ethanol was used as the milling media. In order to obtain an agglomerate-free powder mixture, the resultant slurry was dried with a rotary evaporator in a drying box at 80 °C for at least 5

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Table 1
Phase composition of combustion products for different starting powder (Argon pressure: 0.5 MPa)

Sample	Method	Phase composition of starting powders (wt%.)			Phase composition of combustion products		
		Si	Mo	NH_4Cl	$MoSi_2$	Mo_5Si_3	Free Si
A	SHS	36.93	63.07	0	Major	Trace	Trace
B	SHS	35.45	60.55	4	Extinguished after initiation of wave		
C	COSHS	36.93	63.07	0	Major	Trace	Trace
D	COSHS	35.45	60.55	4	Major	ND[a]	ND

[a] ND, not detectable

h to ensure that the powders were completely free of alcohol. The dried powders were then sieved to 60-mesh for following two separate SHS procedures.

1. Normal SHS procedure

The mixed powders were pressed into a cylindrical graphitic crucible with typical dimensions of 40 mm diameter and 45 mm high. A tungsten coil was placed on the upper surface of the powders. The powders were combusted on a steel chamber under 0.5MPa Ar pressure. The purity of the Ar gas was reported as 99.9%.

2. Chemical oven SHS procedure (COSHS)

The mixtures of Si and Mo were put into inner part of the graphite crucible and mixtures of Si and Ti (atomic ratio Si/Ti =3/5) used as chemical oven were put into outer part shown in Fig. 1. There was carbon felt between inner part and outer part. A tungsten coil located on the upper surface of the powders in outer part. The two mixtures get in touch with each other on the bottom of the graphite crucible. The powders were combusted in a steel chamber under 0.5 MPa Ar (99.9 wt.%) pressure.

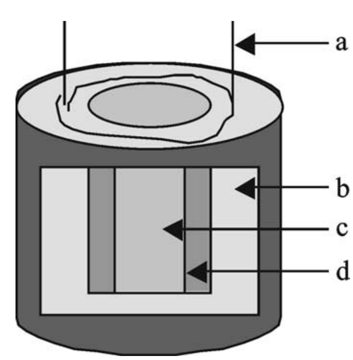

Fig. 1. Schematic of experimental apparatus used for chemical oven combustion synthesis (a) W coil; (b) 3Si+5Ti (atomic ratio); (c) 2Si+Mo (atomic ratio); (d) carbon felt.

The combustion wave was determined from the output of a W-5%Re/W-26%Re thermocouple placed inside a small hole drilled in the side of each specimen. The phase composition of the reaction products was investigated by X-ray diffraction (XRD) using CuK_α radiation. The morphologies of combustion products were studied by using scanning electron microscopy (SEM). X-fluorescence analysis was conducted to examine the impurities in the products.

3. Results and discussion

The temperature profiles obtained both in SHS and COSHS are indicated in Fig. 2. Except Sample B, the other three samples all can be reacted under conditions shown in Table 1. Though sample B has the same composition as sample D, it cannot carry out in normal SHS, because the heat given out by the reaction between Si and Mo is not enough for both sustaining propagation and volatilization of NH_4Cl. In COSHS procedure, additional heat given by the reaction between Si and Ti make NH_4Cl volatilized. The max-

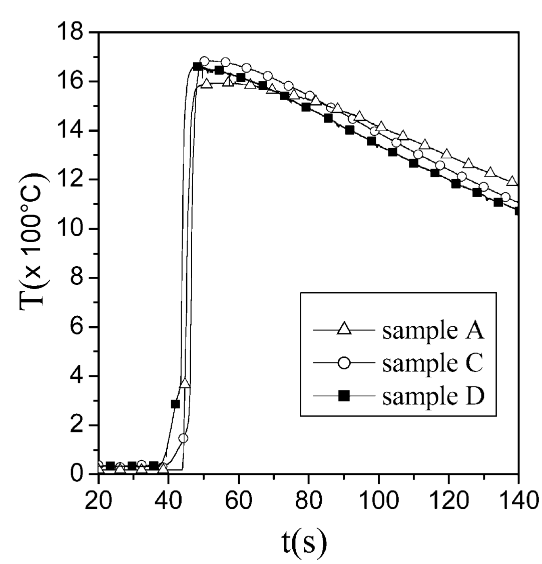

Fig. 2. Temperature profiles of samples A, C and D.

imum temperatures of sample C and sample D recorded in COSHS procedure are 1675 and 1661 °C while the maximum temperature of sample A recorded in normal SHS is 1598 °C, lower by 77 and 63 °C, respectively. As can be clearly seen that the COSHS procedure could produce higher temperature than normal SHS in this work.

The results of XRD patterns of the three samples A, C, D are shown in Table 1. The XRD results of samples A and C show that there are traces Si and Mo_5Si_3 in the products. Sample D was obtained through COSHS procedure by adding 4 wt.% NH_4Cl additives. It can be seen that sample D is pure $MoSi_2$ phase from Table 1. Because of the volatilization of NH_4Cl, it left a great deal of voids in the reactants and let the contact among powders less. It can be predicted the propagation rate is lower and reaction time is longer, then the reaction is thoroughly completed.

The composition of products detected by X-fluorescence analysis is shown in Table 2. It can be seen the products prepared by COSHS are purer than products prepared by normal SHS.

Fig. 3 shows SEM photographs of the combustion products. $MoSi_2$ grains, which agglomerated and formed a three dimensional network structure, were observed in the three samples. It can be seen from Fig. 3c that the products obtained by COSHS with NH_4Cl are more homogeneous and less agglomerated than the other two

Table 2
X-fluorescence analysis of starting powders and combustion products

Element	Composition (wt.%) of starting powders		Compositions (wt.%) of combustion products		
	Si	Mo	Sample A	Sample C	Sample D
Al	0.02	ND[a]	0.03	0.02	0.04
P	ND	1.2	ND	ND	ND
Cl	ND	ND	0.44	0.58	0.57
Ca	0.04	ND	0.06	ND	ND
Cr	ND	ND	0.04	ND	ND
Fe	0.54	ND	0.13	0.10	0.12
Ni	ND	0.06	0.02	ND	0.03
Th	ND	0.16	0.06	ND	ND

[a] ND, not detectable

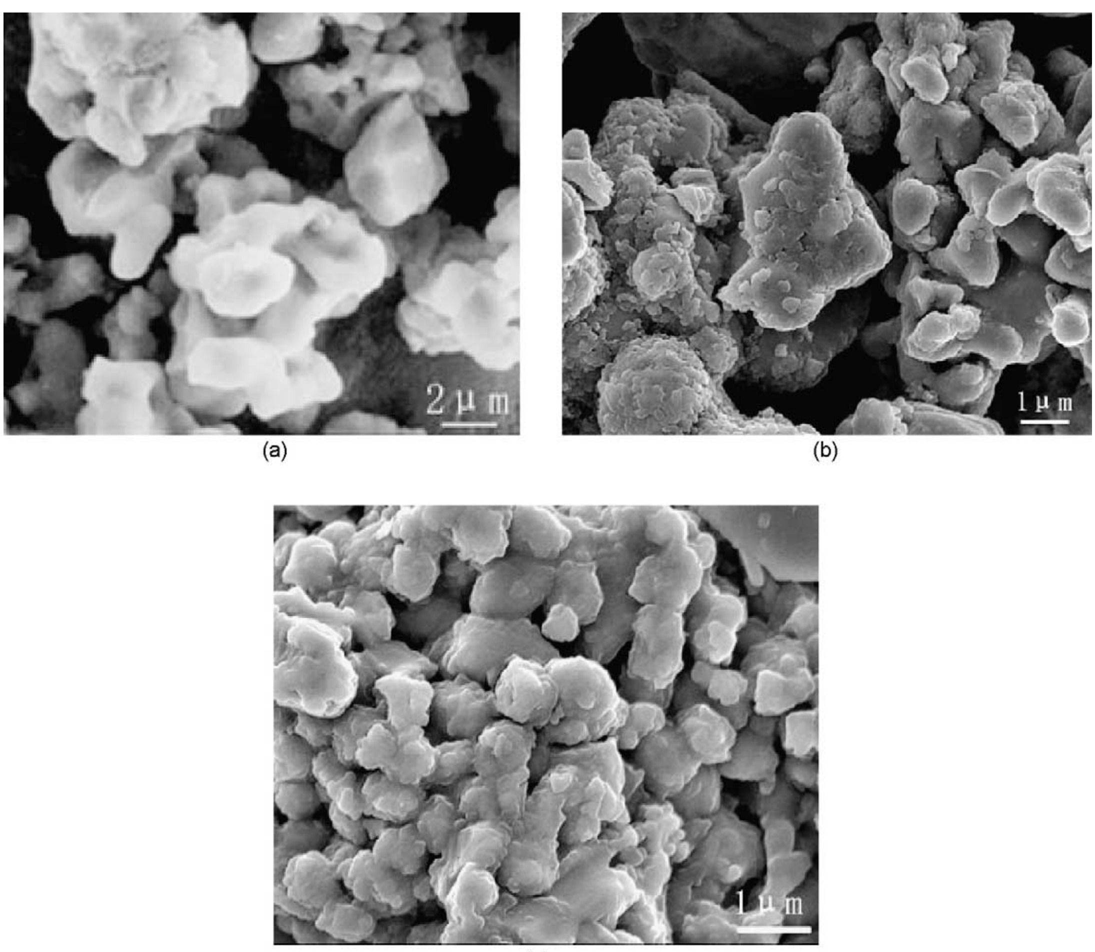

Fig. 3. SEM photographs of combustion products: (a) Sample A; (b) Sample C; (c) Sample D.

samples. Due to the volatilization of NH_4Cl, contact among powders became less and grains grew slowly.

4. Conclusion

High pure single-phase molybdenum disilicide intermetalic was synthesized by ''chemical oven'' combustion synthesis method with adding NH_4Cl additive. The mixed powders of Si and Ti were used as chemical oven to enhance SHS procedure for purifying combustion products. NH_4Cl was added to reactants for controlling grains growth and homogenizing products. The reactants with NH_4Cl cannot be ignited in normal SHS. It can be concluded that this process of combustion synthesis is a potential useful method for preparing some powders that cannot be obtained through conventional SHS.

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