

Neutron Diffraction Study (Mo, W)Si₂ Prepared by Self-Propagating High-Temperature Synthesis

Y. Choi*, Hae S. Shim, Jung S. Lee and Yscheslav Em**

* Sunmoon University, Asan, Chungnam, Korea, 336-840
HANARO Center. KAERI, Daejeon, PO Box 150, Korea 305-600

** Institute of Nuclear Physics, Uzbekistan

Abstract

Neutron diffraction study of (Mo,W)SiO₂ powders was carried out to study the formation mechanism of the silicides. The powders were prepared by self-propagating high temperature synthesis with element powders such as molybdenum, tungsten and silicon in inert argon atmosphere. The combustion behaviors were retarded by adding tungsten. Rietveld refinements of each patterns converged to good agreement($\chi^2=1.88\sim 2.24$). As the tungsten content increases, the lattice parameters of the moly disilicide were changes from $a=0.3204$ nm, $c=0.7844$ nm, $a=0.3206$ nm, $c=0.7841$ nm and $a=0.3207$ nm, $c=0.7839$ nm. The microstructural analysis by scanning electron microscopy and the chemical analysis of the final products by neutron diffractometry indicated that the formation of (Mo, W)Si₂ occurs via dissolution of Mo and W into Si melt followed by silicide precipitation.

1. Introduction

Moly disilicide (MoSi₂) are widely used in industry as electric heating element for their high operating temperature. The electric heating element is commercially manufactured by sintering of the powder mixtures, which powders are generally prepared by heating a Mo and Si powder mixture to temperatures between 1523K and 1673K for 2 to 5 hours followed by milling[1]. The commercial product includes 2-10 vol.% of vitreous SiO₂ phase to prevent oxidation during the reaction and/or milling process. The vitreous SiO₂ phase results in decreasing both the interface bonding strength by providing crack propagation path at ambient temperatures and the high temperature strength by grain boundary segregation in the sintered body. [2] One of possible methods to improve the performance of electric heating element is to add a higher melting point disilicide such as tungsten disilicide which makes complete solid solution with moly disilicide. There are several processing routes to make dense products such as mechanical alloying, reactive sintering, spray forming, and self-propagating high-temperature synthesis (SHS). [3] Among these

processes, the SHS has attracted attention recently because of its various advantages such as high pure products, rapid formation and microstructural controlling without a high temperature furnace.[4] Since the process is characterized by an exothermic heat release sufficient to propagate a combustion front through the powder compact completely consuming the reactant powders once ignition is achieved, the combustion behavior and final composition of product significantly depends on the initial reactant composition. The combustion behavior changing influences formation mechanism and results in producing non-equilibrium phases during the combustion reaction. This causes to understand phase equilibrium and the formation mechanism to better control of the final products. Therefore, phase identification and microstructural observation of the final products with initial composition. The chemical analysis of the final products were carried out by Neutron diffractometry and X-ray diffractometry. The effects of processing variables such as Mo particle size and cooling rate on the (Mo, W)Si₂ particle size were discussed based on the mechanism proposed in this study.

2. Experimental Method

Three types of molybdenum and silicon and tungsten powders (Aldrich, WI, USA) were used in this study. Table 1 is the some selected properties of reactants. Stoichiometric amounts of these powders as shown in Table 2 were weighed on an electron balance inside a glove box with the exposure of less than 0.1 ppm of hydrogen and 0.2 ppm of oxygen. Each powder mix was mechanically blended by a ball mill in an inert argon atmosphere. The mixture was mechanically blended with tungsten by the ball mill in inert argon atmosphere for 1 hour. The ball to powder ratio was 1:5 by weight. The mixed powder was compacted in a steel die into a disk-shaped pellet under 100 MPa pressure. The green pellet was 12 mm in diameter and 25 mm in height. The SHS reaction was carried out like a previous report. [4] The pellet was then placed in a reaction chamber under argon atmosphere. The SHS reaction was ignited by heating the top surface of the pellet with an electric arc for 1 or 2 seconds and the reaction product was cooled to ambient temperature in the chamber prior to examination. The combustion temperature was measured using a thermocouple inserted into the pellet and was recorded by a computer data acquisition system. The propagation speed of the reaction front was measured from the pictures taken by a video camera. The reaction products was analyzed using scanning electron microscope (Jeol 35C), X-ray Diffractometer (Rigaku, Japan). The powder neutron diffraction patterns from 5° to 155° were measured at room temperature using the 32-detector high resolution powder diffractometer (HRPD) at KAERI. Monochromatic neutrons with a wavelength of 0.18339 nm were obtained from a Ge(331) monochromator with a 90° take-off angle. The sample was contained in a cylindrical vanadium can, 8mm in diameter and 40mm in height.

3. Results and Discussion

Fig. 1 shows a X-ray Diffraction spectra of the SHS product prepared by the combustion reaction between molybdenum and silicon. All of the major peaks were found to match with the standard peaks of MoSi_2 from JCPDS card, indicating the formation of monolithic MoSi_2 phase in a matter of seconds via the SHS reaction. Other molysilicide phases such as Mo_5Si_3 , Mo_3Si including unreacted Mo and Si were not detected. This single phase formation through the combustion process is not common. In order to study phase stability in detail, neutron diffraction analysis was carried. Fig 2 is typical neutron diffraction pattern of (W, Mo) Si_2 prepared by self-propagating high temperature synthesis, which neutron diffraction results are summarized in Table 3. The Rietveld refinement of each patterns converged to good agreement ($\chi^2=1.88\sim 2.24$). In the AF sample, the Rietveld refinement of a structural model consisting of the Si_2Mo (79.79%) solid solution, Mo(12.91%) and Si(7.3%) converged to $\chi^2=2.24$. The lattice parameter of the Si_2Mo phase, $a=0.3204$ nm, $c=0.7844$ nm obtained from the Rietveld refinement. In the C sample, the Rietveld refinement of a structural model consisting of the Si_2Mo (23.9%), Si_2W (40.89%), Mo(9.11%), Si(9.16%) and W(16.94%) converged to $\chi^2=1.88$. The lattice parameter of the Si_2Mo phase, $a=0.3206$ nm, $c=0.7841$ nm obtained from the Rietveld refinement. Also, lattice parameter of the Si_2W phase was $a=0.3212$ nm, $c=0.7822$ nm. In the EF sample, the Rietveld refinement of a structural model consisting of the Si_2Mo (52.35%), Mo(15.16%), Si(10.73%) and W(21.75%) converged to $\chi^2=2.54$. The lattice parameter of the Si_2Mo phase was $a=0.3207$ nm, $c=0.7839$ nm.

Fig. 3 is morphologies of final products prepared by SHS reaction with different initial molybdenum particle size of $10\ \mu\text{m}$. The reaction product was of partially sintered and its particle diameters are in a range from 1 to $2\ \mu\text{m}$, which are smaller than that of elemental molybdenum powder. Inner particle size was larger than outer particle size. The microstructure of the SHS products depends on the combustion behavior. Since the reaction heat conducted from the reaction zone would raise the temperature of the nearby reactants up to the melting point of the lower melting point reactant of silicon, the elements with higher diffusivity should diffuse through the product layer for a complete conversion in a few seconds. Since the diffusivity of the elements significantly depends on the temperature, the addition of high melting point such as tungsten results in retarding the formation and changing composition of the products. This supports that molybdenum atoms diffuse out into liquid silicon and occur nucleation on a solid tungsten powders surface followed by heterogeneous nucleation mechanism.[5, 6] Hence the formation mechanism suggested in this study is that silicon and molybdenum powders were melted and supersaturated in liquid phase, and nucleation occurs on solid tungsten powders followed by

the dissolution of tungsten into the nuclei to form complete solid solution.

4. Summary

Neutron diffraction study of (Mo,W)SiO₂ powders prepared by self-propagating high temperature synthesis with different composition of molybdenum, tungsten and silicon was carried out. Tungsten addition retarded the combustion reaction and produced different chemical composition of silicides. Rietveld refinements of each patterns converged to good agreement ($\chi^2=1.88\sim 2.24$). As the tungsten content increases, the lattice parameters of the moly disilicide were changes from $a=0.3204$ nm, $c=0.7844$ nm, $a=0.3206$ nm, $c=0.7841$ nm and $a=0.3207$ nm, $c=0.7839$ nm. morphology of the final products did not depend on initial powder sizes. Form the microstructural analysis by scanning electron microscopy and the chemical analysis of the final products by neutron diffractometry indicated that molybdenum atoms diffuse out into liquid silicon and occur nucleation on a solid tungsten powders surface followed by heterogeneous nucleation mechanism. Accordingly, the proposed mechanism includes that molybdenum and silicon powders were initially melted and supersaturated in liquid phase, and heterogeneous nucleation occurs on solid tungsten powders followed by the dissolution of tungsten into the nuclei to form complete solid solution.

5. Acknowledgement

Authors would like to thank Korea Science Foundation for carrying out this study.

6. References

- [1] I. J. McColm, "Ceramic Science for Materials Technologies", Leonard Hill, 1983.
- [2] Max-Planck Institute, "Powder Metallurgy International", vol. 20(4), pp. 26-28, 1988.
- [3] Ceramic Source Book, vol. 6, 1990-91, The American Ceramic Society, Inc.
- [4] K. Wijayatilleke, Y. Choi, M. E. Mullins, and J. K. Lee, Fine Ceramic Society annual meeting, Boston, MA, August 1983.
- [5] R. Pampuch, J. Bialoskorski and E. Walasek, Ceramics Intern. vol. 13, pp. 63, 1987.
- [6] Y. Zhang and G. C. Stangle, J. of Materials Rev., vol. 10, pp. 962-979, 1995.

Table 1. Some selected properties of reactants

Substances	Mo	Mo	Mo	Si	W
Manufacturer	Aldrich	Aldrich	Aldrich	Aldrich	Aldrich
Purity[%]	99.9	99.9	99.99	99.99	99.9
Average Size [μm]	1	10	75	75	12
Melting Point[$^{\circ}\text{C}$]	2623	2623	2623	1414	3000

Table 2. Composition of reactant powder mixtures

sample #	molar ratio				
	Mo(1 μm)	Mo(10 μm)	Mo(75 μm)	Si(75 μm)	W(12 μm)
A-1	1	-	-	2	-
A-2	-	1	-	2	-
A-3	-	-	1	2	-
B	-	0.5	-	2	0.5
C	-	0.7	-	1	0.3
D	-	0.3	-	-	0.7

Table 3. Typical results of Rietveld refinements of the (Mo, W)Si₂

Phase	Space group	Lattice parameter (nm)	Wt. fraction (%)	R-Bragg	χ^2
Si ₂ Mo	I4/mmm	a = 0.320606(12) c = 0.784169(51)	23.90	3.93	1.88
Si ₂ W	I4/mmm	a = 0.321225(14) c = 0.783319(58)	40.89	3.45	
Mo	Im3m	a = 0.314753(27)	9.11	3.26	
Si	Fd3m	a = 0.543036(17)	9.16	6.07	
W	Im3m	a = 0.316513(27)	16.94	3.59	

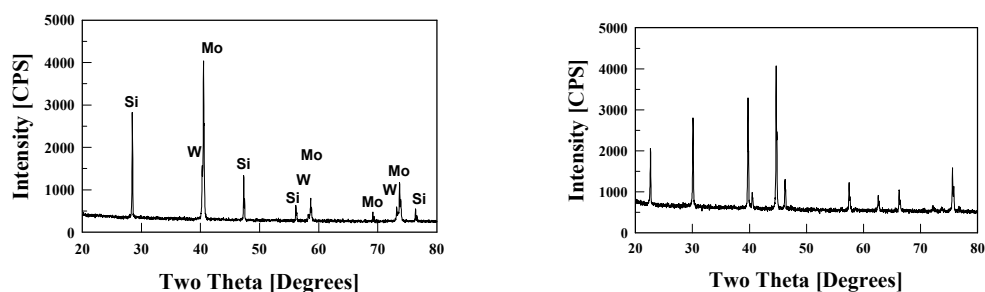


Fig. 1 X-ray spectra of the SHS products with initial composition of 0.7Mo + 0.3W + 2Si (left) before SHS (right) after SHS

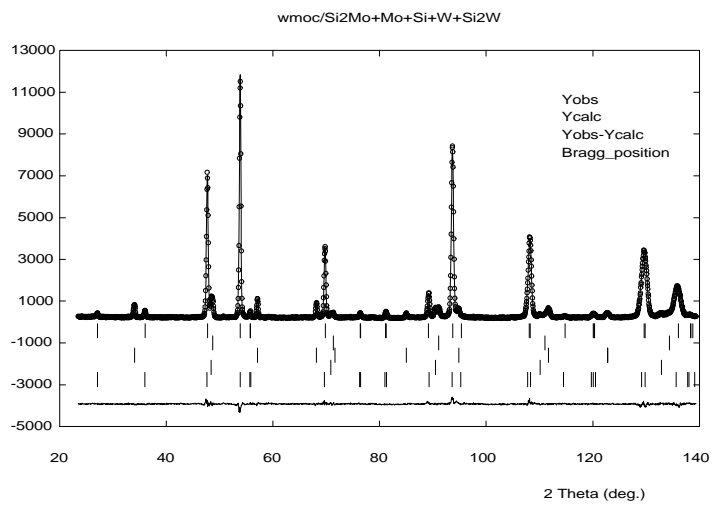


Fig 2. Typical neutron diffraction pattern of $(W, Mo)Si_2$ prepared by self-propagating high temperature synthesis

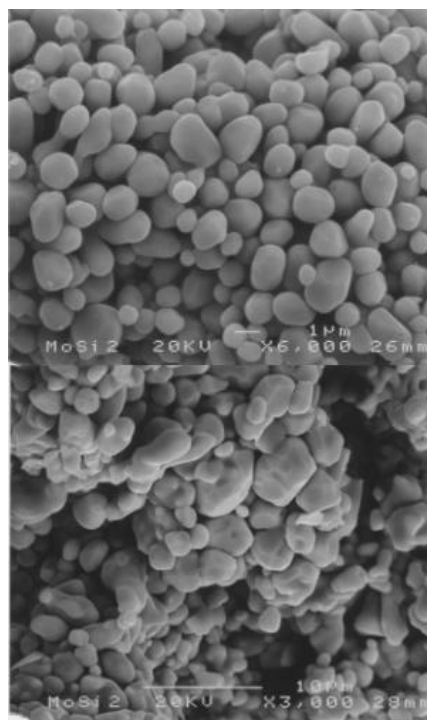


Fig. 3 Scanning electron micrographs of final product with initial Mo size and position (top : outer surface, bottom : inner layer)