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Manufacturing of low cost $MoSi_2/Al_2O_3$ composites by microwave activated self propagating high temperature Synthesis

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In this research, low cost $MoSi_2/Al_2O_3$ composites with various amounts of molybdenum oxide, silica and aluminum were prepared by a microwave activated self propagating high temperature synthesis method. The effect of pressure and microwave radiation time on the physical properties and chemical composition of these composites were investigated. The results showed that for compression of green samples, a maximum density and a minimum porosity can be achieved by applying 300 MPa pressure and increasing the microwave radiation time, would lead to the desired phases and completion of the reaction. After 50 seconds of microwave radiation, the sintering density and hardness would reach the maximum values of 4.75 g/cm^3 and 1015 Vickers respectively.

Key words: Molybdenum disilicide, Microwave, SHS, Composite, MoO_3, SiO_2, Al_2O_3.

Introduction

The self propagating high temperature synthesis method (SHS) which is sometimes called combustion synthesis (CS) is an effective, low-cost method for production of various industrially useful materials. Today SHS has become a very popular method for the preparation of ceramics and composites and is practiced in many countries. Extensive research has been carried out in the last few years, in order to use the SHS method for materials processing, energy saving and environmental protection [1-5].

Over the last decade, silicides have received considerable attention for a combination of properties such as strength, high temperature oxidation and creep resistance. One of the most important silicides is molybdenum disilicide ($MoSi_2$) [6-8]. This compound has been extensively studied during the past 20 years for its high melting point (2020 °C), high electrical conductivity and very good oxidation resistance at high temperatures, even in very aggressive environments [9, 10]. The main limitation for its widespread application at high temperature results from a brittle-to-ductile transition at 900-1000 °C that confers $MoSi_2$ with a very low creep resistance at temperatures higher than 1200 °C. Alumina is an oxide known for its low density (3.98 g/cm^3), high electrical resistivity and excellent creep resistance even at temperatures higher than 1400 °C. The coefficients of thermal expansion (CTE) of $MoSi_2$ and Al_2O_3 are very similar between 20 and 1400 °C. Dense $MoSi_2/Al_2O_3$ composites have already been fabricated by conventional sintering or by combustion synthesis [11].

Microwaves are coherent and polarized electromagnetic waves with a frequency range from 300 MHz to 300 GHz, corresponding to wavelengths of 1 metre to 1 millimetre. When microwaves penetrate and propagate through a material, the internal electric fields generated within the volume of the material induce translational motion in ionic or molecular dipoles. Resistance to these induced motions results in heating of the material. In thick sections of ceramic materials (dielectric materials), penetrating radiation creates hot interiors, enable, internal moisture and internal gases generated during binder burnout to be removed [11]. By exposing a ceramic to microwave radiation, energy would be concentrated inside the sample, and this enables indirect heating, energy distribution or reaction of materials. These features are unique for the microwave method which makes it very attractive for ceramic processing.

On the other hand, in the self propagating high temperature synthesis process, two or several mixed reactants react exothermically in a self-sustaining manner, to form products due to the large difference in free energy and enthalpy between the product and reactants [9-11].

Amrute et al. [12] synthesized MoO_3/SiO_2 composites by a sol-gel method and investigated the catalytic application of this composite. Jokisaori et al., [13] reported the processing of single phase Mo_5Si_3 by microwave activated combustion synthesis. Dumont et al., [14] produced functionally graded $MoSi_2/Al_2O_3$ materials (FGM) with alumina contents varying from 20 to 80 mol%. Most of this research did not emphasis either the quality of the manufactured composites nor the physical properties of the final products.

In this research $MoSi_2/Al_2O_3$ composites were manufactured using microwave ignited SHS and different

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parameters of this method were investigated. In the conventional SHS process, reactants are ignited in a resistance furnace, by a hot filament or by a laser. The novelty of the present method is the usage of microwave energy to initiate the reaction between materials forming intermetallic or ceramic compounds. Furthermore most previous studies were conducted, using pure elements, which are very expensive. In this paper however, fabrication of molybdenum disilicide was done using low cost silica and molybdenum trioxide and aluminum.

Experimental procedure

Molybdenum oxide (MoO_3, 99.9%, 325 mesh), silicon oxide (SiO_2, 99.5%, 325 mesh) and aluminum powder (Al, 99%, mesh 325) were purchased from the MERCK Company. Initially, the three constituents were mixed in stoichiometric (ST) and extra stoichiometric ratio containing excess silica (5 to 15 wt. %) or excess aluminum (5 to 15 wt. %). The powders were ball milled for 2 h with corundum balls to ensure homogeneous mixing. Powders were uniaxialy pressed in a mold for 100 to 900 MPa pressure to 30 mm diameter pellets. The green compacts were ignited in a microwave furnace at 2.45 GHz for about 20 to 50 seconds.

The effect of the chemical composition was studied on stoichiometric (ST) and extra stoichiometric ratio containing excess silica (5 to 15 wt. %) or excess aluminum (5 to 15 wt. %). The chemical composition and fabrication parameters of these samples are shown in Table 1. These compositions were designated as ST (stoichiometric), AST5, AST10, AST15 (with excess aluminum) and SST5, SST10, SST15 (with excess silica). The effect of compaction pressure and microwave radiation time was studied on stoichiometric (ST) samples. The chemical composition and fabrication parameters of these samples are shown in Tables 2 and 3.

X-ray diffraction (XRD) patterns of the samples were measured by a Philips EXPERT diffractometer using Cu-Kα radiation. The final density and porosity of fabricated samples were measured by the ASTM-C20-48 standard. The hardness of the samples was measured by a Shimadzu HMV-200 and the chemical composition of them was evaluated by XRF (ART 8410 Swees) and classic chemical analysis methods.

Table 1. Composition and fabrication parameters of stoichiometric and non-stoichiometric samples (With excess amounts of aluminum or silica).

Sample code	MoO_3%	SiO_2%	Al%	P (MPa)	t (s)
ST	36.92	30.77	32.31		
AST5	34.42	28.27	37.31		
AST10	31.92	25.77	42.31		
AST15	29.42	23.27	47.31	300	40
SST5	34.42	35.77	29.81		
SST10	31.92	40.77	27.31		
SST15	29.42	45.77	24.81		

Table 2. Composition and fabrication parameters of samples with different compaction pressures.

Sample code	MoO_3%	SiO_2%	Al%	t (s)	P (MPa)
STP1					100
STP2					200
STP3					300
STP4					400
STP5	36.92	30.77	32.31	30	500
STP6					600
STP7					700
STP8					800
STP9					900

Table 3. Composition and fabrication parameters of samples with different microwave radiation times.

Sample code	MoO_3%	SiO_2%	Al%	P (MPa)	t (s)
STt20					20
STt30	36.92	30.77	32.31	300	30
STt40					40
STt50					50

Results and Discussion

XRD results of samples with different compositions are shown in Figure 1. Based on this figure, it could be concluded that several secondary phases are present in AST and SST samples. For example unreacted aluminum and SiO_2 exist in AST and SST samples respectively.

As figure 1 shows, that increasing the aluminum content from 5 to 15% (AST5 to AST15 samples), causes free aluminum peaks to appear beside the delayed formation of Mo $(Al,Si)_2$ and $MoSi_2$ phases. This may be related to the decrease of MoO_3 and SiO_2 contents of these samples.

By increasing the SiO_2 content from 5 to 15% (SST5 to SST15), free SiO_2 peaks have been sharpened and in SST15 (15% SiO_2), sharp peak of SiO_2 can be clearly recognized (figure 1). Also by increasing the silica content, the formation of $Mo(Al,Si)_2$ and $MoSi_2$ phases has been delayed. Therefore the desired phases were formed by using the stoichiometric ratio of MoO_3, SiO_2, Al and increasing the percentage of SiO_2 and Al would not have any effect on their formation. This result is the same as a previous study [9].

The effects of compaction pressure on the density of fabricated samples are shown in table 4 and figure 2. As can be seen in table 4 and figure 2, increasing the pressure may lead to three different mechanisms [7]:

1. A decrease of the porosity size and an increase of

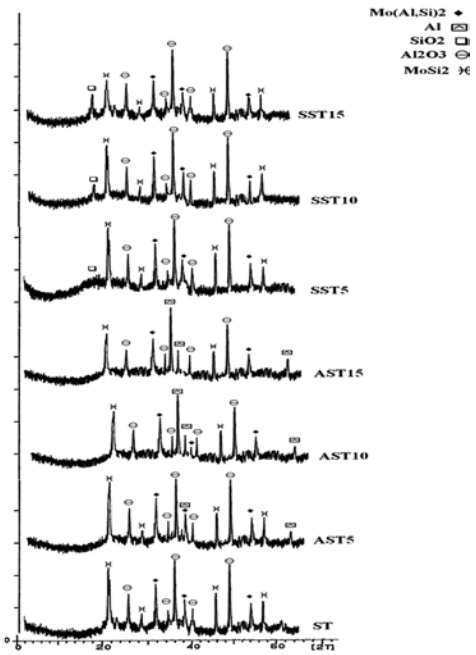

Fig. 1. XRD pattern of $MoO_3/Al/SiO_2$ composites with different ratios of SiO_2 and Al.

Table 4. Effect of compaction pressure on final density and porosity of samples.

Sample code	P (MPa)	Green density (g/cm^3)	Apparent density (g/cm^3)	Porosity (%)
STP1	100	3.17	4.47	13.15
STP2	200	3.55	4.53	11.3
STP3	300	3.74	4.66	8.11
STP4	400	3.81	4.17	12.4
STP5	500	3.88	3.79	16.2
STP6	600	3.93	4.12	15.8
STP7	700	3.98	4.4	15.14
STP8	800	4.13	4.49	14.6
STP9	900	4.28	4.59	13.39

reaction powder contact points will lead to an improved reaction and establishment of the desired phases.

2. A rapid temperature increase may cause sudden expansion of imprisoned gases inside the small pores, which in turn leads to the creation of large pores.
3. If low melting point phases exist in samples, a high pressure may force low melting point phases into the pores which will lead to an increase in density and a decrease in porosity.

The curve in figure 2 consists of 3 regions which may occur based on the above three mechanisms:

Region I obeys mechanism 1, in which the sintering process has been completed by increasing the pressure from 100 MPa to 300 MPa. With a pressure of 300 MPa, the maximum density and minimum porosity have been achieved.

By increasing the pressure above 300 MPa (region

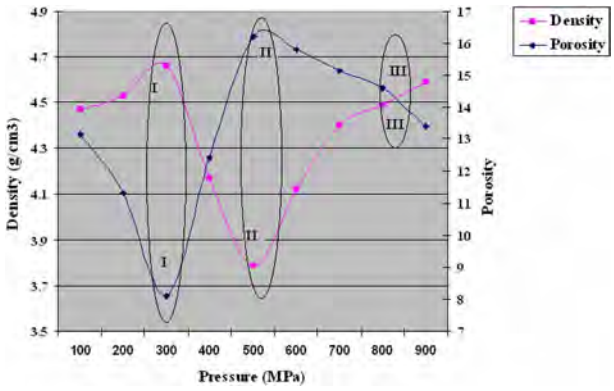

Fig. 2. Effect of pressure on final apparent density and porosity.

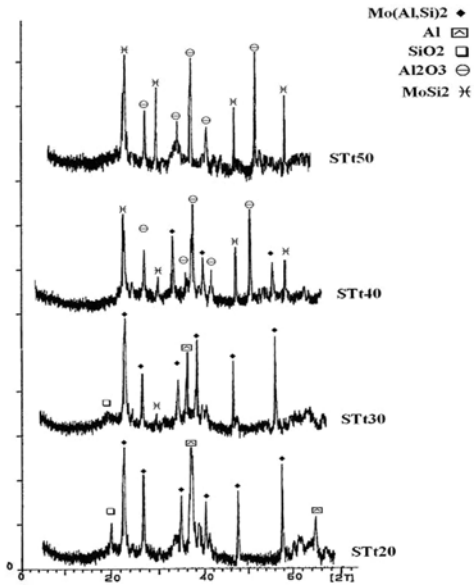

Fig. 3. XRD patterns of $MoO_3/Al/SiO_2$ compositions manufactured with different microwave radiation times.

II), the density decreased and porosity increased. This may be related to the expansion of imprisoned gases creating large pores which follows mechanism 2.

By increasing the pressure up to 500 MPa (region III), the density has increased again. This condition only happens in systems consisting of at least one phase with a low melting point. This phase is melted during microwave radiation and the residual stress inside the system leads the melted phase in to the pores and fills them. This phase is aluminum which has about 660 °C melting point. This mechanism is so complex and needs to be proved by some future experiments. Deevi and Deevi [15] reported that the presence of molten Al is necessary for the synthesis of the composite. Dumont et al. [16] reported that a very fast reaction in preparation of $MoSi_2/Al_2O_3$ composites by SHS begins just after the melting of aluminum.

XRD patterns of $MoO_3/Al/SiO_2$ compositions with a stoichiometric composition manufactured with different microwave radiation times (20 to 50 seconds) are shown in figure 3.

Table 5. Final density and hardness of manufactured composites with different sintering times.

Sample code	Sintering time (S)	Final density (g/cm^3)	Hardness (Vickers)
STt20	20	4.66	960
STt30	30	4.69	985
STt40	40	4.71	1005
STt50	50	4.75	1015

Table 6. Chemical composition of STt20 to STt50 samples.

Sample code	$\%SiO_2$	%Al	Mo $(Al,Si)_2$	$\%Al_2O_3$	$\%MoSi_2$
STt20	9.7	13.9	76.4	-	-
STt30	3.1	5.4	85.6	3.3	2.6
STt40	-	-	15.1	53.4	31.5
STt50	-	-	-	61	39

Table 7. Thermodynamic data of different phases in our study.

Composition	ΔH_{298} (J/mole)	ΔS_{298} (J/mole.°C)
$MoSi_2$	-131796	65.06
MoO_3	-745170	77.78
Al_2O_3	-1677366	51.04
SiO_2	-910438	41.46
Al	0	0

As figure 3 shows, by increasing the microwave radiation time, Al_2O_3 peaks have sharpened and Mo $(Al,Si)_2$, $MoSi_2$ and Al_2O_3 phases have increase. A X-Ray Diffraction (XRD) patterns reveal that all Mo $(Al,Si)_2$ phases have transformed to $MoSi_2$ and Al_2O_3 phases in 50 seconds microwave radiation. Also in order to investigate physical properties of the manufactured samples, the sintered density and the hardness of them have been measured. The results can be seen in table 5.

Based on this table, the sintering density and hardness have been increased by an increase of the sintering time. This may be due to the formation of the $MoSi_2$ and Al_2O_3 phases, which have larger densities and hardnesses than the Al, and SiO_2 phases. These results confirmed the previous results obtained from XRD patterns (figure 3).

By combination of XRD results and some classical chemical analysis methods, the chemical compositions of some fabricated samples were calculated and the results are shown in table 6. Based on this table the amounts of Al_2O_3 and $MoSi_2$ have been increased in STt50 which means that after 50 seconds microwave radiation the reaction is completed.

Considering to raw materials used in the composite manufacturing, one of the 3 reactions below would be possible [7, 10]. In accordance to the XRD and chemical analysis results, and the presence of $MoSi_2$ and Al_2O_3 and absence of Mo, $Al_6Si_2O_{13}$ and Al_2SiO_5 reaction (3) has been suggested for our reaction.

$$4MoO_3 + 3SiO_2 + 8Al \rightarrow 4Mo + Al_6Si_2O_{13} + Al_2SiO_5 \quad (1)$$

$$MoO_3 + SiO_2 + Al \rightarrow Mo(Al,Si)_2 + MoSi_2 + Al_2SiO_5 + Al_2O_3 + Al_6Si_2O_{13} \quad (2)$$

$$3MoO_3 + 6SiO_2 + 14Al \rightarrow 3MoSi_2 + 7Al_2O_3 \quad (3)$$

Also according to the thermodynamic data of elements and compounds which are collected in table 7, the enthalpy of the suggested reaction (3) has been calculated and it is about -1.475.193 J/mole. This enthalpy is considerable and the best driving force for synthesis of $MoSi_2$.

Conclusions

1. $MoO_3/Al/SiO_2$ composites can be manufactured by the microwave initiated SHS method.
2. An increase in percentage of Al and SiO_2 from the stoichiometric ratio would cause a decrease in the formation of the desired phases ($MoSi_2$, Al_2O_3), and extra Al and SiO_2 will remain in the final composition.
3. By increasing the microwave radiation time up to 50 seconds, all the raw materials and intermediate compounds are converted to $MoSi_2$ and Al_2O_3 and the reaction has been completed.
4. The sintering density and hardness respectively reach maximum values of 4.75 g/cm^3 and 1015 Vickers after microwave radiation for 50 seconds.

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