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Effect of Mechanical Alloying on Combustion Densification of $MoSi_2$

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Abstract The effect of the mechanical alloying of elemental Mo and Si powders on the combustion densification behavior of $MoSi_2$ was investigated. The ignition temperature of the combustion reaction of the mechanically alloyed powder was measured to be significantly lower than that of the powder mixture prepared by the low energy ball milling process. The densification of the products after the combustion reaction under compressive pressure from the mechanically alloyed powders, however, was found to be poorer than that of the products from the ball milled powder.

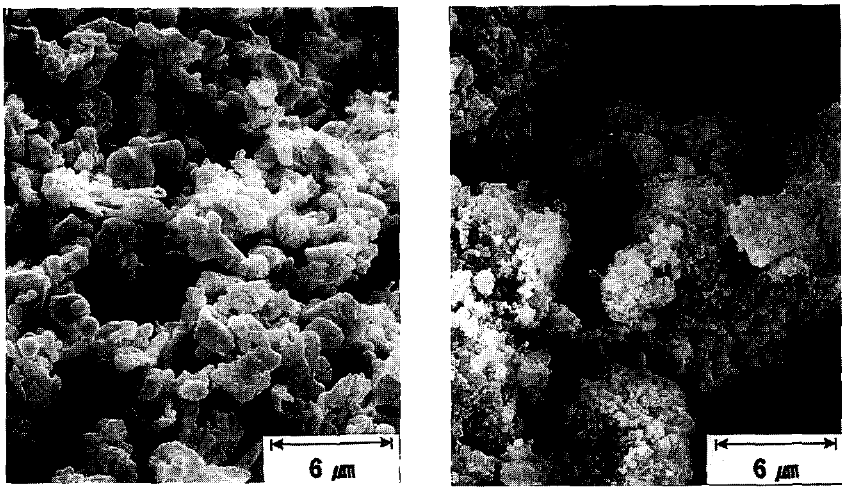
1. Introduction

Combustion synthesis of $MoSi_2$ has attracted much research interests[1-5] in recent years, because of the merits of the process itself as well as the possible application of the materials as structural components at elevated temperatures. The process utilizes the heat of compound formation in synthesizing or/and densifying the product. Combustion synthesis occurs when the reactant is heated up to the ignition temperature. The standard heat of formation of $MoSi_2$ from elemental Mo and Si is 132.3 kJ/mole and can raise the temperature of $MoSi_2$ up to 1800K under the adiabatic condition.[3] The ignition temperature of the combustion reaction of $MoSi_2$ synthesis from elemental Mo and Si powder mixture was measured to be in a range from 1200 to 1410℃.[4] The ignition of the combustion reaction has been attributed to a sudden increase of the contact area between Mo and Si upon melting of Si.[5]

Densification of $MoSi_2$ during the combustion synthesis was attempted either by extruding the sample undergoing the combustion reaction or by applying compressive pressure during the reaction. In those processes, the mold and the reactant must be heated up to the ignition temperature to initiate the combustion reaction, which imposes stringent limits practical applicability of the process. The simultaneous synthesis and densification should be more easily applicable if the ignition temperature is reduced to a temperature range where most of mold materials can withstand the applied pressure. One of the feasible ways to lower the ignition temperature would be to increase the contact area between Mo and Si powders. Thus, in this study an attempt was made to investigate the effects of the mechanical alloying of the elemental powders on the ignition temperature as well as on the densification during the combustion reaction under compressive pressure.

2. Experimental Procedures

The morphologies of Mo and Si powder used in this study are shown in Fig. 1. The size of Mo powder is in a range from 2 to 4 μm and average size of Si powder is 15 μm in diameter. Mechanical alloying using a Spex mill was conducted for 30 minutes to 5 hours. The ball to powder weight ratio was kept at 10. For comparison, elemental Mo and Si powder mixtures were prepared by mixing with a low energy ball milling. The characteristics of the mechanically alloyed powders were analyzed using scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS), X-ray diffraction (XRD),



(a) Mo (b) Si

Fig. 1. SEM micrographs of (a) Mo and (b) Si powders used in this study.

and laser particle size analyzer. The temperature profiles of the samples undergoing the combustion reaction were measured by a Pt-Rd type thermocouple (R-type) inserted in the reactants. The densification ebehavior of the mixture during the combustion reaction under compressive pressure was investigated in a hot press. The pressure was changed from 10 to 80 MPa and the heating rate to the ignition temperature was kept at 50℃/min. The density of the reaction product was measured by the Archimedian method.

3. Experimental Results and Discussions

3.1. Combustion Densification of Mo and Si Powder Mixture

Fig. 2 shows a SEM micrograph of the fractured surface of the sample after the combustion reaction using the as-mixed Mo+2Si powder mixture. The reactant was heated up to 1400℃ to initiate the combustion reaction without any compressive pressure applied. Heavy agglomeration and large pores were noted from the micrograph. The agglomeration has been attributed to the partial melting of $MoSi_2$ during the combustion reaction since the combustion temperature of the reaction reaches the melting temperature.[5] Several factors have been attributed responsible for the pore formation, which include volume shrinkage during the compound formation, porosity from the reacting powder compact, trapping of volatile gases generated during the reaction, etc.

Fig. 2. Fractured surface of $MoSi_2$ powder compact produced by thermal explosion mode.

Fig. 3 shows the micrograph of the sample after the combustion reaction under a compressive pressure of 70 MPa. Densification of the product was enhanced with the application of the compressive pressure, but large pores are still observed from the products. The grain size of the products was around 30 μm. Since the large grains might be detrimental for the densification due to the interlocking during

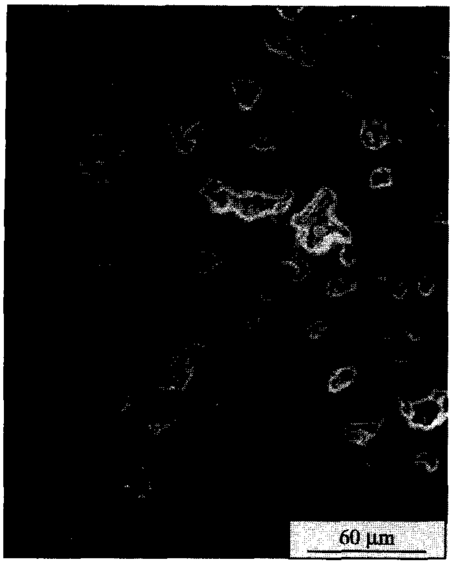


Fig. 3. SEM micrograph of $MoSi_2$ reacted under a 70 MPa pressure.

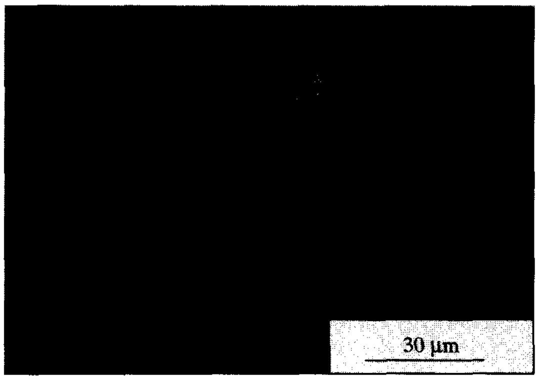


Fig. 4. SEM micrograph of Mo+(0.1Al+1.9Si)-20%$MoSi_2$ reacted under a 70 MPa pressure.

the rearrangement period, pre-synthesized $MoSi_2$ powder as well as aluminum powder were added to refine the $MoSi_2$ grain size. Fig. 4 shows the micrograph of Mo+(0.1Al+1.9Si)-20%$MoSi_2$ powder mixture after the combustion reaction under a 70 MPa pressure. The density of the sample was improve to more than 99% of the theoretical density and only fine pores with spherical shape remained in the sample. The pores should be due to the gas trapped in the sample. These results show that the theoretical densification could be achieved for the reactant with alloy addition as well as the nucleation agents. This densification, however, was achieved by heating the sample up to 1400℃, which severely limits the practical applicability of the process. Thus in this study, mechanical alloying of the reaction mixture was conducted in order to lower the ignition temperature of the combustion reaction.

3.2. Mechanical Alloying of Mo and Si Powder

Fig. 5 shows the microstructures of the powders mechanically alloyed for various times. After 30 minutes of alloying, fine particles are randomly mixed together. As the alloying time increases, the lamella structure that usually observed during the mechanical alloying of ductile metal powders was formed. EDS analysis on the microstructure indicated that the white phase is Mo and the black phase Si. The lamella structure between Mo and Si is unexpected since the brittle to ductile transition temperature of Si is above 800℃. It would be unrealistic to assume that the Si powder to deform plastically to form the laminated microstructure during the mechanical alloying even considering temperature rise during the milling. SEM micrograph of the Si phase of the laminated structure at a higher magnification is shown in Fig. 6. Although the Si phase at the lower magnification seems to be a continuous phase, this figure revealed that the Si phase in the lamella structure is an agglomeration of very fine discrete Si particles in actual. The high impact energy of the mechanically alloying process seems to breakdown the brittle Si phase to ~20~100 nm in diameter and forms the lamella structure with elongated ductile Mo phase. The very fine Si particles seem to be cold-welded partially together to form a macroscopically continuous phase as seen in Fig. 5.

Fig. 7 shows XRD patterns of the powders mechanically alloyed for various milling times. $MoSi_2$ peak intensities increased with milling time, indicating that $MoSi_2$ is formed during the mechanical alloying process. The amount of $MoSi_2$ formed during the mechanical alloying was estimated by cali-

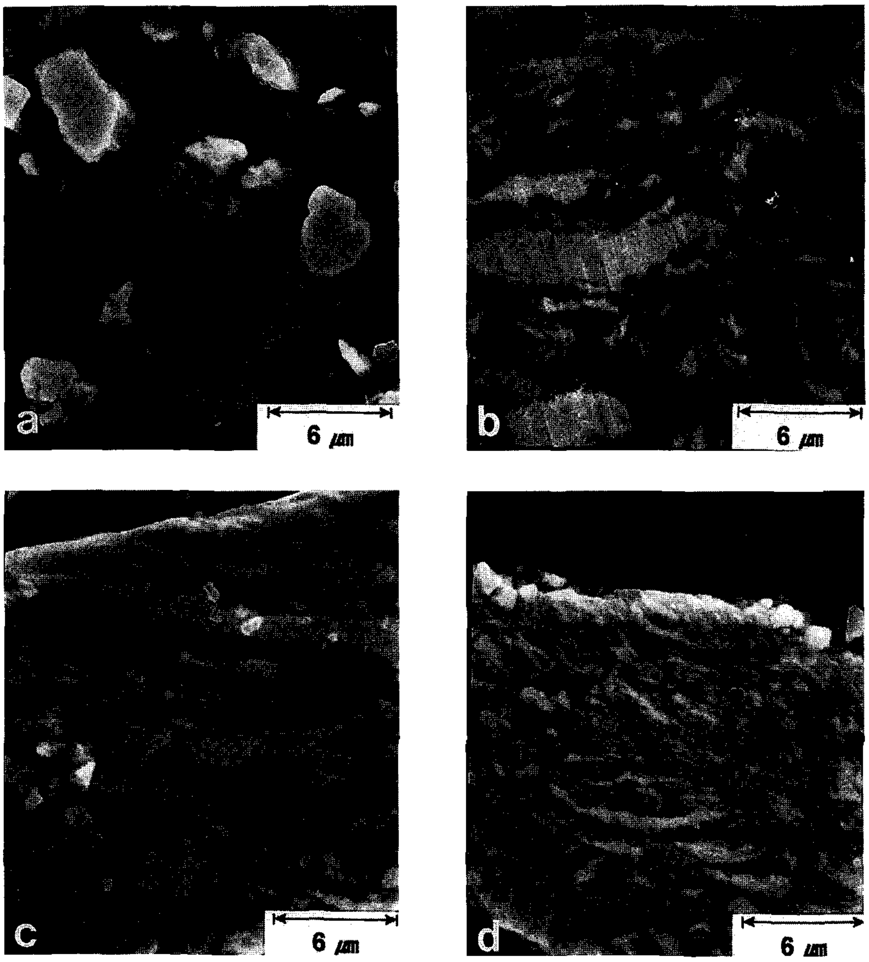


Fig. 5. SEM micrographs of the powders mechanically alloyed for (a) 30 min, (b) 1 hour, (c) 3 hours, and (d) 4 hours.

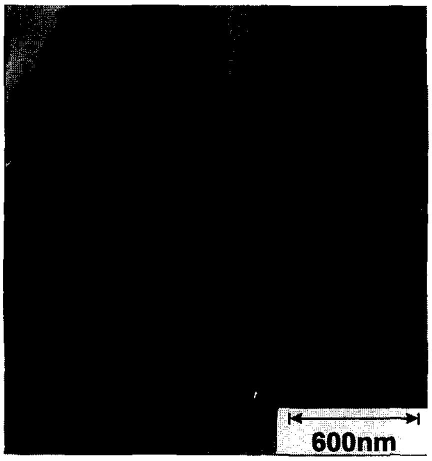


Fig. 6. SEM micrograph of Si layer mechanically al- **loyed for 1 hours.**

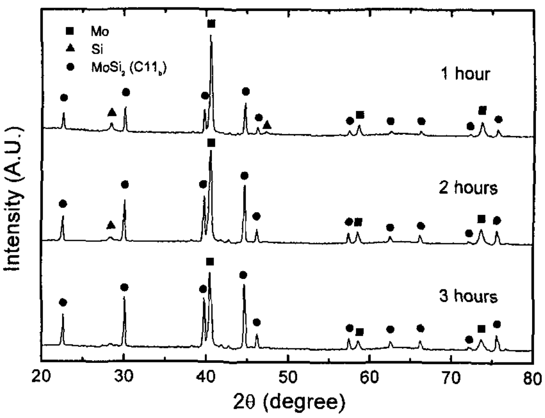


Fig. 7. XRD patterns of the powders mechanically al- **loyed for (a) 1 hour, (b) 2 hours and (c) 3 hours.**

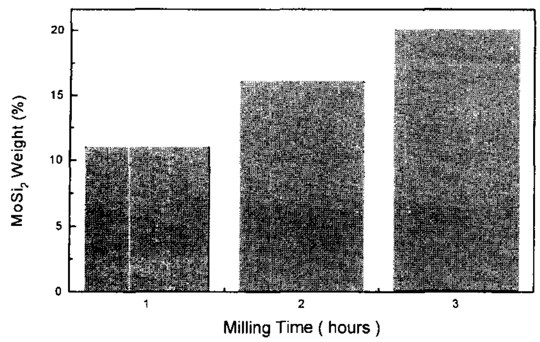


Fig. 8. Fraction of $MoSi_2$ formed during the mechanical alloying process.

brating the XRD peak intensity ratio between Mo and $MoSi_2$ phases. Fig. 8 shows the fraction of $MoSi_2$ formed with the alloying time. After 3 hours of mechanical alloying, 20% of Mo and Si powders were converted to $MoSi_2$.

3.3. Effect of mechanical alloying on the combustion reaction and densification

The temperature profiles of the mechanically alloyed powders while heated in a furnace are shown in Fig. 9. The compacts of the powders mechanically alloyed for 30 minutes to 3 hours did not shown any exothermic peaks until heated to 950℃. The ignition temperature of the samples must be higher than 950℃. On the other hand, the compact with 4 hour milling shows a sharp exothermic peak around 670℃, indicating the ignition of the combustion reaction. The ignition temperature is significantly

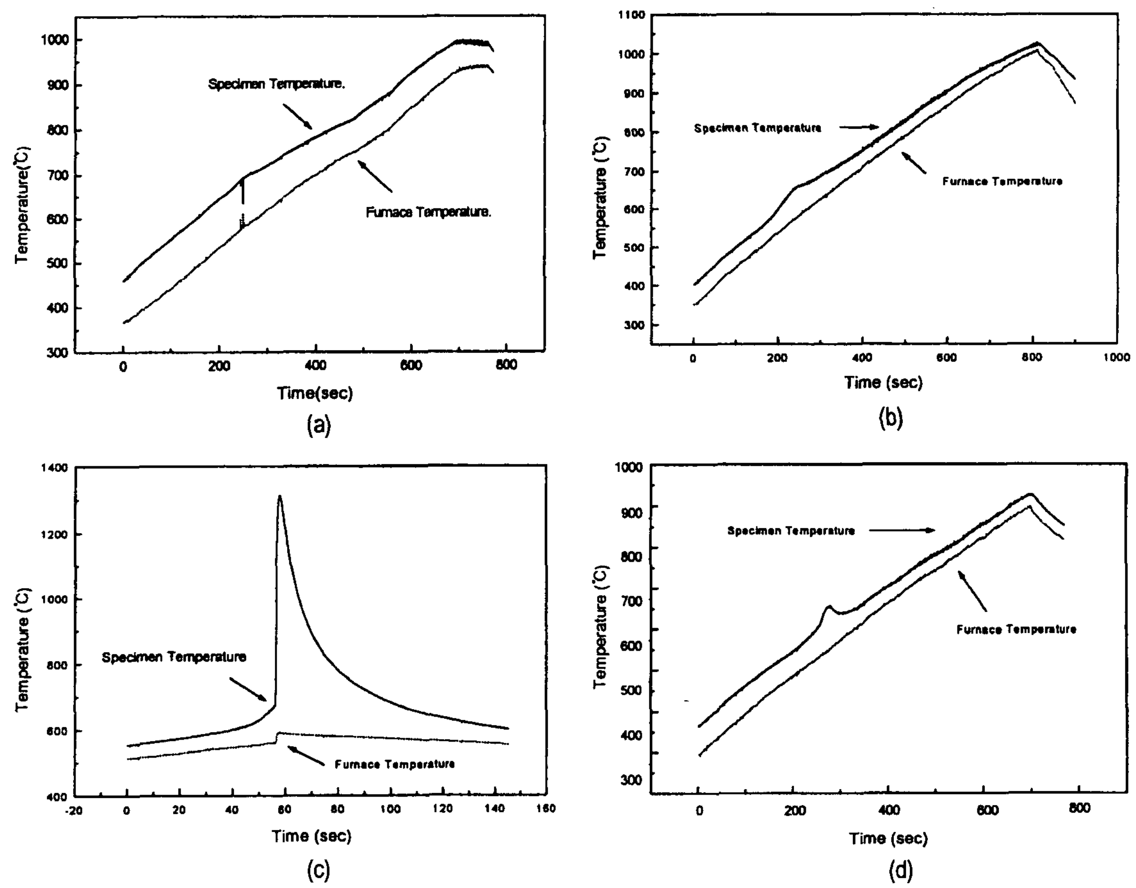


Fig. 9. Temperature profiles of the samples while heated in a furnace. The reactants were mechanically alloyed for (1) 2 hours, (b) 3 hours, (d) 4 hours, and (d) 5 hours.

lower that that of the ball mill mixed sample, which is in the range from 1200 to 1410℃. There might be several factors that contribute to the decreased ignition temperature; increased contact area between Mo and Si, stored strain energy in the powder, etc. Among the factors, the increased contact area should play a major role in decreasing the ignition temperature. The stored energy in the Si powder would be relatively small because Si is very brittle. The larger contact area should increase diffusion flux between the reacting powders, which in turn increases the generation rate of heat of reaction and finally leads to the ignition of the reaction.

The combustion temperature of the sample, on the other hand, was measured to be lower than that of $MoSi_2$ formed from elemental Mo and Si. The combustion temperature of the reaction of the sample preheated to 670℃ is calculated to be the melting temperature of $MoSi_2$(2030℃),[5] but the measured combustion temperature was 1600℃. This decreased combustion temperature should be either due to the experimental errors such as lack of contact between sample and thermocouple or due to the dilution effect of the $MoSi_2$ phase formed during the mechanical alloying. The temperatures measured in this experiment showed quite reproducible with an error range +/-25℃. The $MoSi_2$ phase formed during the alloying should reduce the heat of formation per unit volume of the sample and this should effectively decrease the combustion temperature. The compact of the powder mechanically alloyed for 5 hours, on the other hand, did not show any sharp exothermic peak until heated up to 950℃. This phenomenon seems to manifest the effect of the dilution effect of $MoSi_2$ phase formed during the mechanical alloying. Since the fraction of $MoSi_2$ increases with milling time as in Fig. 8, the formation heat liberated per unit volume of reactant should decrease with the milling time. Thus as the fraction of the MoSi2 formed is increased above a critical limit, the formation heat released would not be enough to support a self-sustained combustion reaction. A previous study showed that the wave propagation mode of combustion reaction could not be initiated as the volume fraction of $MoSi_2$ diluent is increased to 20%.[5]

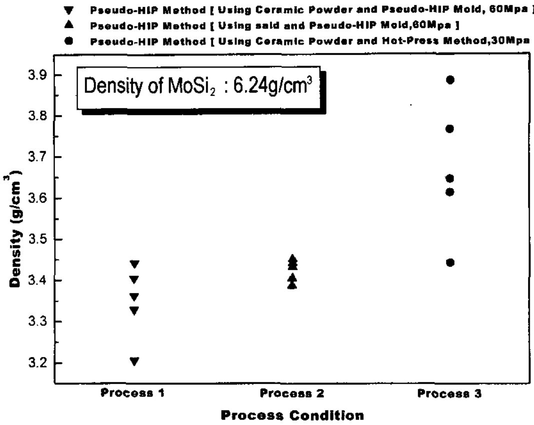


Fig. 10. Density of sample after combustion densification using the mechanically alloyed powders.

Combustion densification of the mechanically alloyed powders was conducted under a compressive pressure ranging from 20 to 80 MPa. Fig. 10 shows the density of the reaction products. Microstructural observation of the samples indicated that very little densification has occurred in the sample. This lack of densification seems to be related with the low combustion temperature of the sample. As shown in Fig. 9, the combustion temperature was measured to be around 1600℃, which is much lower than the melting temperature of $MoSi_2$.

4. Conclusions

Combustion reaction of Mo+2Si powder mixtures prepared by a low energy ball milling process under a compressive pressure resulted in the dense $MoSi_2$ phase. The reaction was initiated at the temperatures ranging from 1200 to 1400℃. The ignition temperature was found to be decreased significantly upon using the Mo+2Si powder mixtures prepared by mechanical alloying. The mechanical alloying of the powders resulted in the formation of the lamella structures. The reactant mixture, however, was not densified with the compressive pressure due to low combustion temperature.

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