Microstructure and Mechanical Properties of MoSi$_2$–X (X = Al, B, Nb) Alloys Fabricated by MA-PDS Process

Aidang Shan, Wei Fang, Hitoshi Hashimoto and Yong-Ho Park

National Institute of Advanced Industrial Science and Technology, AIST, Tohoku, Sendai 983-8551, Japan

In order to improve the mechanical properties of MoSi$_2$ alloys, alloys with Al, B or Nb addition were prepared by an advanced consolidation process that combined mechanical alloying with pulse discharge sintering (MA-PDS). Their microstructure and mechanical properties were investigated. The microstructure of MoSi$_2$ alloys fabricated by the MA-PDS process was much finer than that of the sample sintered from the commercial MoSi$_2$ powders. Alloys made from powders milled in Ar gas had fewer silica or alumina phases as compared to their counterparts sintered from powders milled in air, presumably because of the suppression of the oxidation process during milling in Ar gas. Both Vickers hardness and tensile tests indicated that the alloys fabricated by the MA-PDS process showed better performance than the sample sintered from commercial MoSi$_2$ powders because of the finer grain sizes. The Al-added alloy sintered from the powders milled in air gave the best mechanical properties due to the suppression of SiO$_2$ and formation of fine Al$_2$O$_3$ particles.

(Received July 23, 2001; Accepted November 6, 2001)

Keywords: MoSi$_2$ alloy, mechanical alloying, pulse discharge sintering, microstructure, mechanical property

1. Introduction

Intermetallic compounds such as aluminides and silicides have drawn a great attention for the high-temperature structural applications. Over the past twenty years, researchers have studied many alloy systems and processing routes to select potential intermetallic compound for applications at high temperatures. MoSi$_2$, which has been widely used as a heating element due to its excellent oxidation resistance at high temperatures, is one of the candidate materials. It has a high melting point (2323 K) and low density (6.24 Mg/m$^3$). However, the poor room temperature ductility and low high temperature strength need to be improved for applications as structural materials.

Recent attempts have been concentrated on the development of MoSi$_2$ composites in order to overcome the problems of monolithic MoSi$_2$. The second phase reinforced MoSi$_2$ composites showed an increase of their mechanical properties. The addition of SiC, ZrO$_2$ or TiC to MoSi$_2$ has made a significant improvement in high-temperature flexural strength and room temperature fracture toughness. Also, the incorporation of ductile reinforcements such as filaments or whiskers of refractory metals showed a similar enhancement in toughness. However, a major problem of using ductile metals was the strong reaction of these reinforcements with matrix phases. The application of diffusion barrier coating on the metallic reinforcements was found to be successful in reducing the reaction.

Alloying is one of the most widely adopted methodologies to improve the mechanical properties of the intermetallic compound. Attempts had been made on MoSi$_2$ with a variety of alloy elements such as W, V, Re, Cr, Nb, Al, and B. Aluminum addition was found to be extremely effective in eliminating the grain boundary amorphous silica phase, a vital detriment to the high-temperature creep resistance of MoSi$_2$ alloys. This process is called “in-situ deoxidation”, through which aluminum reacted with silica to form alumina and elemental silicon. The resultant microstructure is a mixture of MoSi$_2$ phase and alumina phase. More aluminum addition results in a new phase, Mo(Si, Al)$_2$ which has a C40 crystal structure. So aluminum additions will not only modify the oxide phase, but also produce significant alternations to the matrix phase itself through alloying. Such an effect provides many metallurgical possibilities for controlling the microstructure and mechanical properties of MoSi$_2$ alloys. Nb is also an interesting alloy element for MoSi$_2$. A theoretical analysis has revealed that Nb, when substituting for the Mo atoms in MoSi$_2$, will help to increase the ductility of the alloy. An experimental work has also shown that Nb is effective in increasing the room temperature deformability and the high-temperature strength of single crystal MoSi$_2$. Boron has been added to MoSi$_2$ to make a bid for the strengthening. Many borides have much higher hardness. For example, α-MoB phase has a Vickers harness of 23–24.5 GPa and Mo$_2$B$_5$ phase has a Vickers hardness value of 23 GPa. These values are significantly higher than that of monolithic MoSi$_2$ phase, having generally no more than 10 GPa. For alloys in the previous experiments have been mostly made with arc melting or hot isostatic pressing with somewhat coarse powders as the starting materials, namely some microns or some tens of microns in particle size, the yielded microstructures contain grains with some tens micron size. A recent work by Niihara and Suzuki shows that very fine grain size will give a significant improvement in strength to the MoSi$_2$ monolithic alloy as well as MoSi$_2$ matrix composite with SiC as reinforcement. A room-temperature fracture strength of as high as 1200 MPa was obtained with 15%SiC reinforcement. In their research, MoSi$_2$ alloy or composites are made by hot-pressing of raw MoSi$_2$ powders with particle size of around 1 micron. The sintered bodies have a microstructure with grain size of no more than 5 micron. Up to now it is not yet clear to what extent a fine microstructure will have a beneficial effect on the mechanical properties of the alloyed MoSi$_2$ compound. Mechanical alloying and pulse-discharge-sintering (MA-PDS) method have been proved to be efficient in getting a fine microstructure in MoSi$_2$ intermetallic
compound. In the present study, mechanical alloying was used to produce $\text{MoSi}_2$ and $\text{MoSi}_2\cdot X$ ($X = \text{Al}, \text{B} \text{ or Nb}$) alloy powders from the mixtures of pure elemental powders. The powders were consolidated by the pulse discharge sintering process to maintain the fine grain size of the powders. Microstructures and mechanical properties were investigated. Emphasis was put on the effect of milling atmosphere (air and Ar) on the resulted microstructure and mechanical properties.

2. Experimental Procedure

The nominal compositions for this study were $\text{MoSi}_2$-$3\text{–}10$ at\% $X(X = \text{Al}, \text{B} \text{ or Nb})$. The particle sizes of Mo and Si were less than 3 $\mu$m and 74 $\mu$m respectively, and the purities were 99.9\% and 99\%, respectively. The size of both the added elements, Al and Nb, was less than 48 $\mu$m and B was less than 10 $\mu$m. Their purities were 99\%, 99.9\% and 99.9\%, respectively. The mechanical alloying was conducted as follows: The powders mixed into the desired composition were put into the milling container in air or inside a glove box where Ar gas was continuously circulated. Milling was carried out in a vibratory ball mill with a frequency of 25 Hz and an amplitude of 2.5 mm. The milling time was 200 hours. The cylindrical stainless steel container had an inner diameter of 120 mm and a height of 120 mm. Hardened steel balls with a 25.4 mm diameter were used and the mixed powders were loaded with a ball/powder ratio of 75/1. The mechanical alloyed powders were filled into a graphite mold and were pre-pressed at room temperature. After pre-pressing, sintering was carried out in pulse discharge sintering equipment under a pressure of 55 MPa at 1673 K. The detailed configuration of the pulse discharge sintering equipment can be found in our ear-
lier report.\textsuperscript{19} The microstructure of the sintered samples was examined with a Scanning Electron Microscope (SEM) and the synthesized phases were identified by X-Ray-Diffraction (XRD) method. Vickers hardness test was carried out. Specimens with a gauge section of 1.5 mm × 2 mm × 10 mm for the tensile test were cut from the sintered compacts with an electric discharge machine (EDM). Tensile tests were performed under a cross head speed of 0.05 mm/min at room temperature and 1273 K. The fracture surfaces after tensile tests were observed using SEM.

3. Results and Discussion

3.1 Microstructures

Figures 1 and 2 show SEM micrographs and X-ray diffraction patterns, respectively, of four materials mechanical alloyed in air and in argon gas. The materials are: monolithic MoSi\textsubscript{2} (denoted by MoSi\textsubscript{2}), MoSi\textsubscript{2}–3 at\%Al (denoted by 3Al), MoSi\textsubscript{2}–5 at\%B (denoted by 5B) and MoSi\textsubscript{2}–5 at\%Nb (denoted by 5Nb). The XRD analysis reveals that the MoSi\textsubscript{2} alloys consisted of three phases: MoSi\textsubscript{2} matrix phase (photographed as gray in Fig. 1), silicon oxide in (photographed as black) and Mo\textsubscript{5}Si\textsubscript{3} phase (photographed as white). It is also obvious from Fig. 1 that the sample milled in air included much more Mo\textsubscript{5}Si\textsubscript{3} and silica phases than its counterpart milled in Ar gas. The Mo rich Mo\textsubscript{5}Si\textsubscript{3} phase might be formed due to the deficiency of silicon as a result of the reaction with oxygen during milling. This process would shift the stoichiometric Mo–Si phase equilibrium to the two-phase region of MoSi\textsubscript{2} + Mo\textsubscript{5}Si\textsubscript{3}. Although this reaction would lead to production of SiO\textsubscript{2} phase there was not any corresponding peak in the XRD analysis shown in Fig. 2. This is presumably because the SiO\textsubscript{2} phase appeared amorphous.

For the 3Al alloy, the alumina phase was substituted for the silica phase on the MoSi\textsubscript{2} alloy. The black phase was confirmed to be alumina by Energy Dispersive Analysis of X-ray (EDAX) under SEM. As shown in Table 1, the EDAX results clearly show that the black area contains higher oxygen and aluminum content than silicon content. It is suggested that the addition of Al suppressed the formation of SiO\textsubscript{2} through an \textit{in-situ} deoxidation process.\textsuperscript{14} The reaction can be described in the following formula:

\[
4\text{Al}(\alpha_{\text{Al}}) + 3\text{SiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Si}(\alpha_{\text{Si}} \text{ in MoSi}_2 \text{ or Mo}_{x}\text{Si}_{y}\text{Al}_z)
\]

This reaction has been earlier reported by Silva and Kaufman.\textsuperscript{20} \(\alpha_{\text{Al}}\) is the activity of Al in pure form or in solution in MoSi\textsubscript{2} or Mo–Si–Al alloy. \(\alpha_{\text{Si}}\) is the activity of Si in MoSi\textsubscript{2} or Mo–Si–Al alloy. In the Mo–Al–Si ternary phase diagram shown in the paper by Silva and Kaufman three-percent aluminum addition will change the alloy into a ternary phase, that is, C\textsubscript{11b} + C\textsubscript{40} + Si phase. But in the XRD and SEM examinations the Si and C\textsubscript{40} phases were not observed, only C\textsubscript{11b} phase was observed. This result may come from the fact that the aluminum reacted with silica was not included in the matrix as shown in the phase diagram.

From the SEM photos it can be seen that the alumina particles in the sample sintered from powders milled in air are larger and occupy bigger volume percentage as compared to their counterpart milled in Ar. These results clearly indicate that the sample sintered from powders milled in air has higher alumina content compared to that from samples milled in Ar. As for Mo\textsubscript{5}Si\textsubscript{3} phase, the percentages are quite lower than that in the monolithic MoSi\textsubscript{2} sintered from powders milled in air. This observation yields that aluminum addition has prevented the silicon deficiency during milling in air. We may suggest that during the milling aluminum was oxidized preferentially and prevented the oxidation of silicon, although the detailed mechanism is not clear now.

In the case of 5B, a large difference was found between the microstructures of the samples sintered from powders milled in Ar and in air. Firstly, the sample sintered from powders milled in Ar includes fewer percentage of silica phase compared to that sintered from powders milled in air. This is in agreement with the former explanation for the MoSi\textsubscript{2} monolithic alloy. Secondly, Mo\textsubscript{5}Si\textsubscript{3} appears in the sample sintered from powders milled in air while MoB appeared in the sample sintered from powders milled in Ar.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Phases</th>
<th>Mo</th>
<th>Si</th>
<th>O</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSi\textsubscript{2}–3Al</td>
<td>Black</td>
<td>3.4</td>
<td>7.6</td>
<td>50.8</td>
<td>38.2</td>
</tr>
<tr>
<td>MoSi\textsubscript{2}–5B</td>
<td>White</td>
<td>60.08</td>
<td>38.52</td>
<td>1.4</td>
<td>—</td>
</tr>
</tbody>
</table>
amples sintered from powders milled in Ar. The MoB phase was identified by XRD analysis. It is worthy of note that the MoB phase shows rod-like morphology in contrast to the Mo$_5$Si$_3$ phase that is often equi-axial. It is not clear why such a big difference exists between the samples with the different milling conditions.

In the case of 5Nb, the sample sintered from the powders milled in Ar has a finer microstructure as compared to its counterpart. (Mo$_x$Nb$_{3-x}$)Si$_3$ phase was identified in both the samples. This is in agreement with the result in our earlier report. Both (Mo$_x$Nb$_{3-x}$)Si$_3$ and silica phases are larger in the air-milled samples. And the silica phase volume fraction is also higher in the former. In the XRD pattern of the 5Nb alloy there are also some peaks show the NbSi$_2$ phase that has a C40 crystal structure. This more clearly appears in Ar-milled samples. But the SEM photo does not show any contrast for NbSi$_2$, probably due to the C40 phase has a composition like (Mo$_x$Nb$_{3-x}$)Si$_3$ which is the same as the C11$_b$ matrix phase.

### 3.2 Mechanical properties and fracture behavior

Figure 3 represents the Vickers hardness of the four materials. For comparison, the hardness of MoSi$_2$, MoSi$_2$-X (X = Al, B or Nb) alloy fabricated by MA-PDS process under the same temperature. The hardness values of the samples fabricated by MA-PDS process were higher than that of the sample sintered from commercial powders. As a general rule, the samples sintered from the powders milled in air showed higher hardness as compared to those of milled in Ar. The Al added sample sintered from powders milled in air had the highest hardness. For the samples sintered from the powders milled in the Ar atmosphere, monolithic MoSi$_2$ gave the highest hardness, so it may be suggested that the addition of X was not effective in the increase in hardness.

Figure 4 presents the fracture stress at room temperature for the four materials milled in Ar gas together with the alloy sintered with commercial powders. One exception is the 3Al alloys which were milled respectively in air and in Ar gas. For the pure MoSi$_2$ alloy, the fracture stress values of the samples fabricated by MA-PDS process were higher than that of the sample sintered from commercial powders due to the finer grain size. The 3Al sintered from the powders milled in air showed the highest fracture stress as well as hardness while 5Nb showed the lowest one for the samples sintered from powders milled in Ar.

The fractographies of the tensile specimens are demonstrated in Fig. 5. The sample made from commercial powders was fractured in a transgranular mode. The monolithic MoSi$_2$ made by MA-PDS process also shows a transgranular mode. This observation is in agreement with the results in an earlier research. Although the precise grain size measurement is difficult from the SEM photos, a rough estimation reveals that the grain size of all the MA-PDS alloys are around or below 1 micron. In all the alloys with X additions, a mixed fracture mode was observed. In Al doped MoSi$_2$ alloys the predominant occurrence of intergranular fracture has been reported for the materials with much larger grain size (around 40 micron). All the samples were fractured at stresses less than 300 MPa. However, when the microstructures were compared with each other, the fracture stress did not correspond with the microstructures. As for the 5Nb alloy, the tensile fracture strength attains to only about 150 MPa. This value is significantly lower than bending strengths which are generally above 400 MPa for MA-PDS process synthesized MoSi$_2$-Nb alloys. Such a big difference in fracture strength implies that the fracture stresses are determined by voids formed by imperfect sintering or some defects originated from machining. Another possibility is the residual stress causing micro cracks.

Figure 6 shows fracture stress values tested at 1273 K for MoSi$_2$, 3Al, 3B, 5B and 10B fabricated by MA-PDS process. The fracture stress of MoSi$_2$ sintered from the commercial powders is also shown. The samples fabricated by MA-PDS process gave higher fracture stress than the sample sintered from commercial powders. The 3Al sample sintered from the powders milled in air resulted the highest fracture stress value, namely over 400 MPa. The SEM fractograph of the 3Al sample (milled in air) after the tensile test at 1273 K is exhibited in Fig. 7. The morphology of the fracture surface looks like a ductile fracture mode. However, the sample did not show clear yielding up to the fracture during the tensile test. From this fractograph, it can also be seen that the fine Al$_2$O$_3$ particles were well dispersed. Therefore, the high fracture strength of the 3Al alloy may be attributed to the distribution of fine Al$_2$O$_3$ particles.
Microstructure and Mechanical Properties of MoSi$_2$–X (X = Al, B, Nb) Alloys Fabricated by MA-PDS Process

Fig. 5 SEM micrographs of fracture surface after tensile test of MoSi$_2$ and MoSi$_2$–X (X = Al, B or Nb) alloy fabricated by MA-PDS process. (a) MoSi$_2$ made from commercial powders, (b) 3Al milled in air, (c), (d), (e), (f) are those of 5B, pure MoSi$_2$, 3Al and 5Nb milled in Ar gas.

Fig. 6 Fracture stress values of MoSi$_2$ and MoSi$_2$–X (X = Al or B) alloy fabricated by MA-PDS process. The tensile test is carried out at 1273 K. The fracture stress of MoSi$_2$ sintered from commercial powders is also shown in the figure.

Fig. 7 SEM micrograph of fracture surface after tensile test of MoSi$_2$–3 at%Al alloy fabricated by MA-PDS process with powders milled in Air. The tensile test is carried out at 1273 K.

4. Summary

(1) The microstructure of MoSi$_2$ alloys fabricated by the MA-PDS process was much finer than that of sample sintered from the commercial MoSi$_2$ powders. Alloys made from powders milled in Ar had fewer silica or alumina phases as compared to their counterparts sintered from powders milled in air, presumably because of the suppression of the oxidation process during milling in Ar.

(2) The MoSi$_2$ alloys fabricated by the MA-PDS process showed high hardness values due to their fine grain sizes. The hardness of the sintered alloys made from the powders milled in air was much higher than that of the samples made from the powders milled in Ar because of the higher volume fraction of oxides.

(3) From the tensile test results at ambient temperature...
and 1273 K, the Al added MoSi2 made from powders milled in air had a higher fracture stress due to the suppression of SiO2 formation and the formation of fine Al2O3.

Acknowledgments

The financial assistance extended by the Science and Technology Agency (STA), JISTEC, Japan to A. Shan is gratefully acknowledged.

REFERENCES