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Author(s)	MATSUURA, Kiyotaka; OHMI, Tatsuya; KUDOH, Masayuki; KAKUHASHI, Takashi; HASEGAWA, Tohru
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RESEARCH REPORT

Reactive sintering of molybdenum alumino-silicide and its oxidation resistance

Kiyotaka MATSUURA*, Tatsuya OHMI*, Masayuki KUDOH*
Takashi KAKUHASHI** and Tohru HASEGAWA**

An intermetallic compound, molybdenum alumino-silicide, $\text{MoAl}_x\text{Si}_{2-x}$, is produced from a mixture of molybdenum, aluminum and silicon powders by using a pseudo-hot-isostatic-pressing (PHIP) process and a reactive sintering method. The mechanical properties at room temperature and oxidation behavior at 773 K and 1500 K are investigated. The increase in the PHIP pressure leads to a remarkable increase in density and hardness of the alumino-silicide. The increase in aluminum content of the alumino-silicide leads to a slight increase in density, but it does not affect the hardness. The increase in aluminum content of the alumino-silicide dramatically improves its oxidation resistance.

Keywords: powder metallurgy, reactive sintering, combustion synthesis, intermetallic compound, molybdenum disilicide

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1. Introduction

Molybdenum disilicide, MoSi_2 , is one of the most promising potential structural materials used at ultra-high temperatures up to 1873 K¹⁾. Its excellent properties include a high melting temperature of 2293 K²⁾, a low density of 6.25 Mg/m³ and a high yield strength of 1500 MPa at room temperature³⁾. Although the strength decreases as temperature increases, the strength at high temperatures has been improved by reinforcement with the addition of ceramic particles such as carbide or boride particles^{3),4)}.

The oxidation resistance of molybdenum disilicide at high temperatures is also excellent, because a thin continuous film of amorphous silica, SiO_2 , forms on the surface of molybdenum disilicide at the beginning of oxidation and protects it from further oxidation. However, Maruyama et al.⁵⁾ pointed out that cristobalite, which is crystallized from amorphous silica, is easy to peel off from the surface of molybdenum disilicide because of the volume change due to the phase transformation at a temperature between 436 K and 548 K, and therefore they suggested that alumina, Al_2O_3 , may be a better protecting film than silica, because alumina has a higher melting temperature, chemically more stable properties and no phase transformation.

In this study, we produce molybdenum alumino-silicide,

$\text{MoAl}_x\text{Si}_{2-x}$ ⁶⁾, from the mixture of molybdenum, aluminum and silicon powders by using a reactive sintering method^{7),8)} and a pseudo-hot-isostatic-pressing (PHIP) process^{9),10)}, and investigate the effects of aluminum content on the mechanical properties and oxidation resistance of the alumino-silicide.

2. Procedure

Because the fundamentals of the present experimental procedure are similar to those detailed in our previous papers^{11),12)}, the outline of the procedure is described below.

Molybdenum powder (99.98% pure, 3 μm in diameter), silicon powder (99.999%, 45 μm) and aluminum powder (99.8%, 100 μm) were mixed with the addition of a small amount of ethanol and paraffin. The aluminum content was varied from 0 to 33.3 at%, while the molybdenum content was constant at 33.3 at%. The powder mixture was cold-pressed into a cylindrical compact in a metal mold at a pressure of 320 MPa. The diameter and height of the green compact were 32 mm and 43 mm, respectively.

Type B thermocouple (Pt-30 mass% Rh/Pt-6 mass% Rh) with a diameter of 0.5 mm was used to measure the temperature of the compact during the PHIP process. A thermocouple well (3.5 mm in diameter and 10 mm in

* Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University (Sapporo-shi, Hokkaido).

** Graduate Student, Graduate School of Engineering, Hokkaido University (Sapporo-shi, Hokkaido).

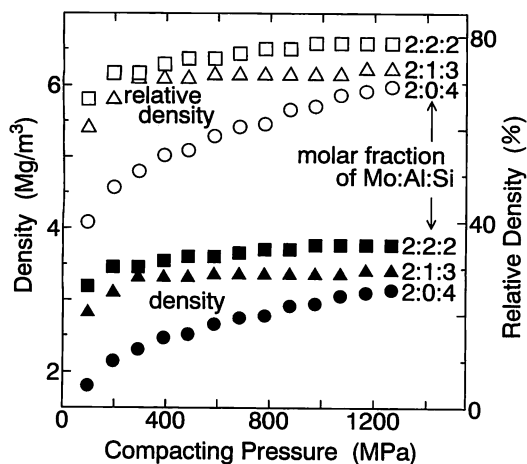


Fig. 1 Effect of compacting pressure on the density of green compact.

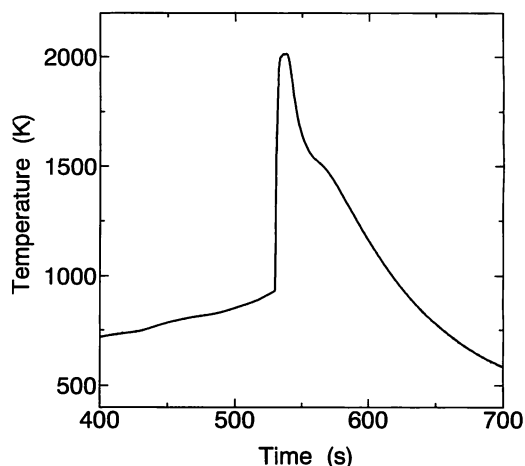


Fig. 2 Change in compact temperature during the PHIP process. Aluminum content: 10 at%.

depth) was drilled from the bottom surface of the compact, and the thermocouple covered with an alumina tube (3 mm and 2 mm in outer and inner diameters) was inserted into the well.

After heating wire of an Fe-23 mass%Cr-6 mass%Al alloy (1.0 mm in diameter) was wound onto the side surface of the cylindrical green compact, the compact was placed in a PHIP vessel (50 mm in inner diameter and 80 mm in depth). The compact was pressed pseudo-isostatically at a pressure of 130 MPa through a pressing medium of alumina powder (0.5 mm in diameter) and was then heated by applying electric power to the heating wire. After 180 s passed from the onset of the exothermic reaction of combustion synthesis^{7),8)}, which had been monitored through sudden increase in temperature, the sample was removed from the PHIP vessel.

The synthesized sample was used for the observation of the microstructure, the analysis of the composition of phases and the measurement of the density, hardness and oxidation resistance. An electron probe microanalyzer (JXA-8900M, JEOL) was used to analyze the composition of the phases. The density was evaluated by Archimedes' method, the hardness by a Vickers hardness tester with an applied load of 98 N, and the oxidation resistance by the weight gain after exposure to air at 773 K or 1500 K.

3. Results and discussion

3.1 Green compact

Fig. 1 shows the effect of the compacting pressure on the density of the green compact. The aluminum content was varied from 0 to 33 at%, while the ratio of Mo:(Al+Si) was constant at 1:2. To investigate the effect of the compact-

ing pressure on the density of the green compact over a wide range of pressure up to 1200 MPa, we used a smaller metal mold (16 mm in inner diameter) compared with that used to produce the green compact to be reactive-sintered.

As the compacting pressure increases to approximately 300 MPa, the density of the green compact sharply increases. However, when the pressure exceeds 300 MPa, the increase in density becomes levelling off, especially for the powder mixture containing aluminum. Therefore, we used a compacting pressure of 320 MPa to produce the green compact to be reactive-sintered afterward. This low pressure of 320 MPa makes it possible to enlarge the green compact to 32 mm in diameter under the maximum load of the press. A larger size for the green compact is preferable from the view point of heat loss, because the pressing medium consumes some of the heat from the exothermic reaction of the combustion synthesis.

Fig. 1 also shows the effect of the aluminum content of the powder mixture on the density of the green compact. Both the density and relative density increase with aluminum content. The relative density is the ratio of the real density to the ideal one. The ideal density of the green compact is evaluated from the density and content of the three elements. The increase in the relative density in Fig. 1 indicates that the volume fraction of the pore decreases with the increase in aluminum content. It is considered that the aluminum powder, which is extremely soft compared with the other two elements, plastically deforms to fill the pore under the compacting pressure.

3.2 Reactive sintering

Fig. 2 shows the change in temperature of the compact during the PHIP process. The nominal content of aluminum of the compact was 10 at%. When the compact is heat-

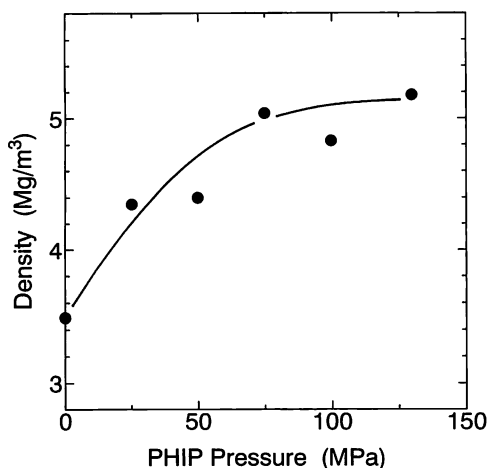


Fig. 3 Effect of PHIP pressure on the density of synthesized molybdenum aluminosilicide. Aluminum content: 33 at%.

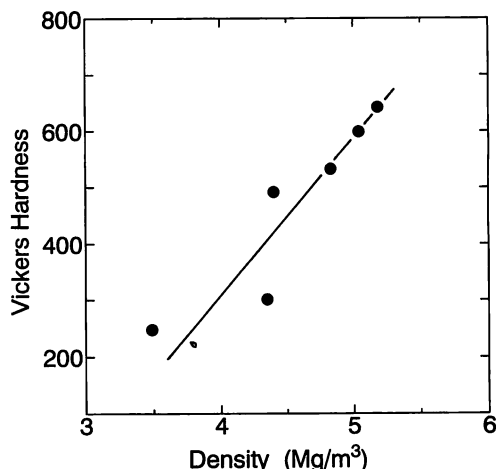


Fig. 5 Relation between density and Vickers hardness of synthesized molybdenum aluminosilicide. Aluminum content: 33 at%.

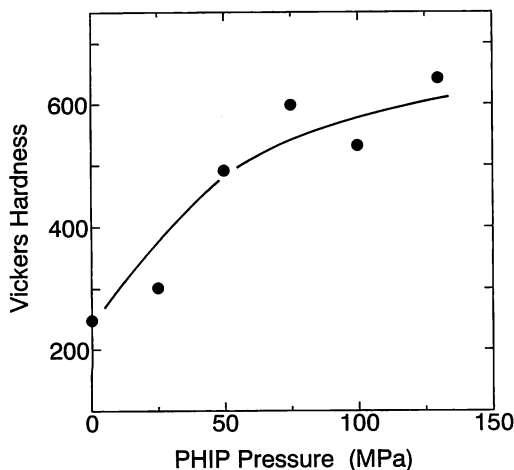
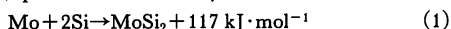


Fig. 4 Effect of PHIP pressure on Vickers hardness of synthesized molybdenum aluminosilicide. Aluminum content: 33 at%.

ed to approximately 920 K, the temperature abruptly increases to approximately 2010 K. Because an electron probe microanalysis indicated that the sample consisted of a monophase structure and that the composition was 32 at% Mo-11 at% Al-57 at% Si, the sudden increase in temperature is considered to have resulted from the exothermic reaction of the synthesis of molybdenum aluminosilicide.

According to Miyamoto¹³⁾, the maximum temperature is calculated to be 1779 K, when the reaction presented in Eq. (1) proceeds adiabatically.



This calculated temperature is lower than the maximum temperature shown in Fig. 2.

3.3 Density and hardness

Fig. 3 shows the effect of the PHIP pressure on the density of the synthesized molybdenum aluminosilicide. The aluminum content is 33.3 at%. The density increases with the pressure. According to the results shown in Fig. 1, approximately 20% of porosity was included in the green compact of this composition. The increase in density results from the removal of the pore, which was achieved by pressing the compact at such high temperatures as observed in Fig. 2.

Fig. 4 shows the effect of the PHIP pressure on the Vickers hardness of the synthesized molybdenum aluminosilicide. The aluminum content is 33.3 at%. The hardness increases with the pressure. It is suggested that the increase in hardness results from the increase in density, because the density and hardness are in a good correlation, as shown in Fig. 5.

Fig. 6 shows the effect of aluminum content on the density of the green compact and the synthesized molybdenum aluminosilicide. The compacting pressure of the green compact is 320 MPa, and the PHIP pressure is 130 MPa. The density of the synthesized molybdenum aluminosilicide is approximately 2 Mg/m³ higher than that of the green compact, and very slightly increases with the aluminum content.

Fig. 7 shows the relationship between the aluminum content of the synthesized molybdenum aluminosilicide and the Vickers hardness. The PHIP pressure is 130 MPa. The hardness of molybdenum aluminosilicide is not affected by the aluminum content. Fig. 3 to Fig. 5 showed that the hardness of molybdenum aluminosilicide increases with the density. Since Fig. 6 showed that the density increases with the

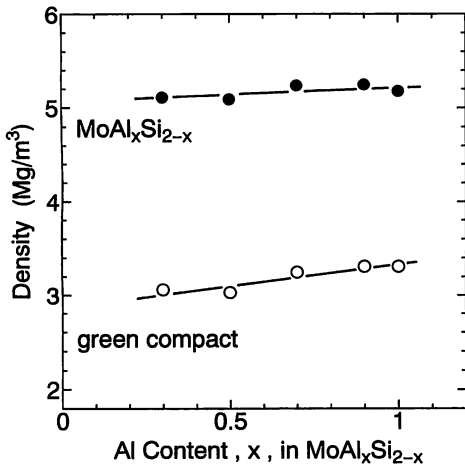


Fig. 6 Effect of aluminum content on the density of synthesized molybdenum aluminosilicide. The PHIP pressure is 130 MPa.

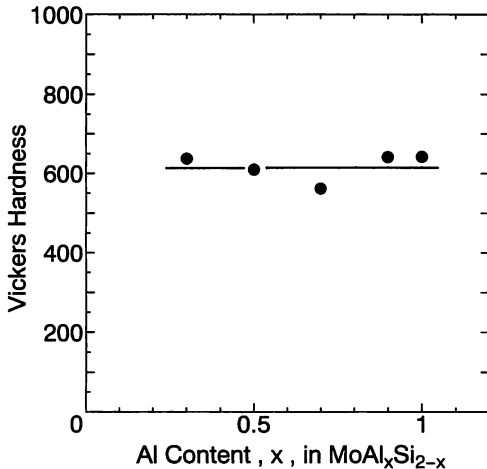


Fig. 7 Effect of aluminum content on Vickers hardness of synthesized molybdenum aluminosilicide. The PHIP pressure is 130 MPa.

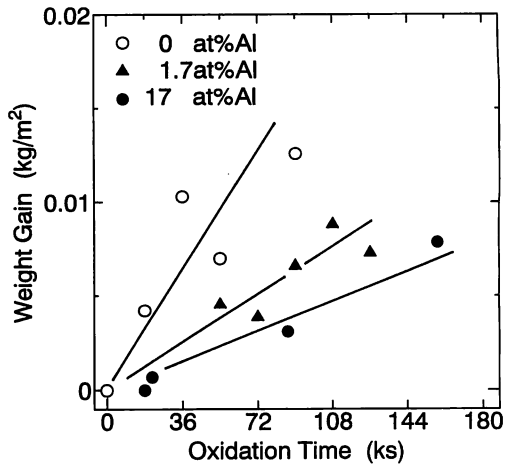


Fig. 8 Increase in weight gain per unit surface area of synthesized molybdenum aluminosilicide during oxidation at 773K in air.

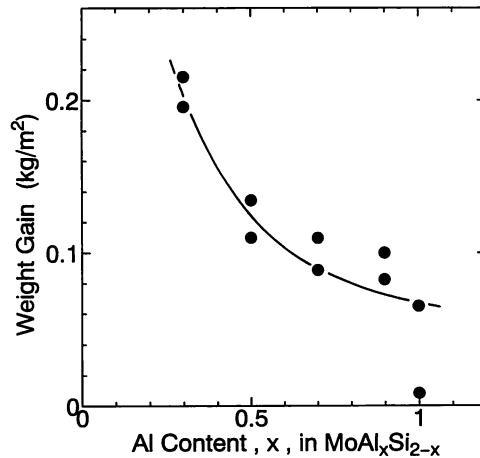


Fig. 9 Effect of aluminum content on weight gain per unit surface area of synthesized molybdenum aluminosilicide after oxidation at 1500 K for 18 ks in air.

aluminum content, we expected that the hardness would also increase, but it did not increase as shown in Fig. 7. It is likely that the increase in hardness is very slight compared with the variation of the experimental error.

3.4 Oxidation behavior

Fig. 8 shows the increase in weight gain per unit surface area of the synthesized molybdenum aluminosilicide during oxidation at 773 K in air. The aluminum content is varied from 0 to 17 at%. It is known that when molybdenum disilicide is heated to a temperature between 673 K and 823 K, accelerated oxidation called "pest"¹⁴⁾ can occur. The "pest" phenomenon is characterized by the linear increase in weight gain with oxidation time, as shown in Fig. 8. Be-

cause the gradient of the line decreases as the aluminum content increases, it is suggested that the addition of aluminum is effective in preventing "pest".

Fig. 9 shows the effect of aluminum content on the oxidation property at 1500 K. The samples were exposed to air for 18 ks at 1500 K. The weight gain significantly decreases with the increase in aluminum content. To consider the reason why the oxidation resistance of the sample is improved by the addition of aluminum, the distribution of the elements was investigated by using an electron probe microanalyzer.

Fig. 10 shows (a) a scanning electron microscope image on a section perpendicular to the surface of the oxidized

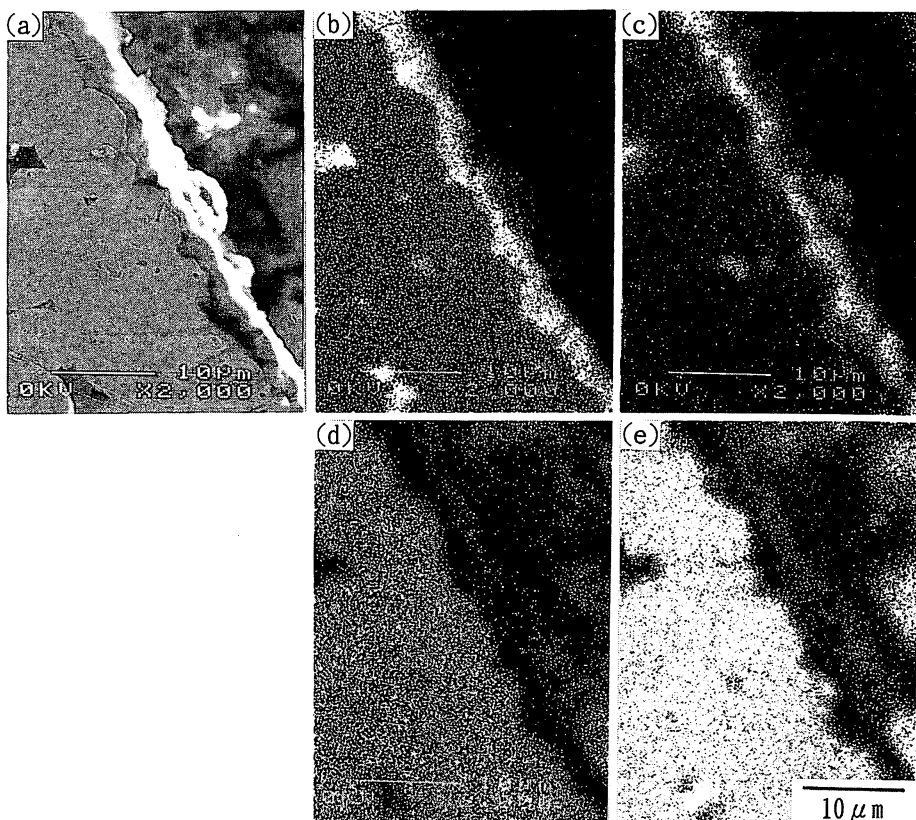


Fig. 10 (a) Scanning electron microscope image on a section perpendicular to the surface of synthesized molybdenum aluminosilicide and X-ray images showing the qualitative distributions of (b) aluminum, (c) oxygen, (d) molybdenum and (e) silicon.

molybdenum aluminosilicide and X-ray images showing the qualitative distributions of (b) aluminum, (c) oxygen, (d) molybdenum and (e) silicon. It is clear that the oxide film formed on the surface of the sample is composed of almost only aluminum and oxygen. It is well known that silica is formed when molybdenum disilicide is oxidized. The results in Fig. 10, however, indicate that aluminum in the sample is selectively oxidized and an alumina-type oxide is formed. This is reasonable, because the standard formation free energy of alumina is much lower than that of silica¹⁵⁾. According to Kurokawa¹⁶⁾, the growth of alumina scale is rate-controlled by the diffusion of aluminum from the base material through the scale to the surface, while the growth of silica scale is rate-controlled by the diffusion of oxygen from the surface through the scale to the base material. The diffusion coefficient of aluminum in alumina is much smaller than that of oxygen in silica at temperatures below 1600 K¹⁷⁾. Thus, the weight gain by oxidation decreases with the increase in aluminum content, as shown in Fig. 9.

4. Conclusions

We produced an intermetallic compound of molybdenum aluminosilicide, $\text{MoAl}_x\text{Si}_{2-x}$, from the mixture of molybdenum, aluminum and silicon powders by using a reactive sintering method and a pseudo-hot-isostatic-pressing (PHIP) process, and investigated its mechanical properties at room temperature and oxidation behavior at 773 K and 1500 K. The results are summarized as follows:

- (1) The increase in PHIP pressure leads to a remarkable increase in density and hardness.
- (2) The increase in aluminum content leads to a slight increase in density, but it does not affect the hardness.
- (3) The increase in aluminum content dramatically improves the oxidation resistance at both 773 K and 1500 K.

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