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Synthesis of $Mo(Si,Al)_2$ alloy by reactive hot pressing at low temperatures for a short time

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$Mo(Si,Al)_2$ alloy was prepared by reactive hot pressing at low temperatures for a short time under 20 MPa in a vacuum using $MoSi_2$, Mo and Al as starting powders. At 1160 °C, 5 min of soaking time was enough to obtain a high density alloy. At 1060 °C, however, 10 min was needed. The formation of $Mo(Si,Al)_2$ was accompanied by the melting of aluminum and controlled by the dissolution of molybdenum into the aluminum melt. It was proposed that the oxygen present in $MoSi_2$ raw powder would react with aluminum and form Al_2O_3 in an amorphous or poor crystallization state. The mechanical properties of the alloy were a little stronger than those of monolithic $MoSi_2$ alloy. The formed Al_2O_3 particles acted as crack-pinning elements, but a large toughening effect could not be obtained by this crack-pinning because of the strong interface bonding and the similar thermal expansion coefficients of $Mo(Si,Al)_2$ and Al_2O_3.

1. Introduction

Molybdenum disilicide ($MoSi_2$), which is commonly used as a heating element, is currently considered to be a candidate for high temperature structural materials for use below 2000 K. It has been reported that the addition of aluminum and formation of $Mo(Si,Al)_2$ could improve the mechanical properties and oxidation resistance of $MoSi_2$ [1, 2]. The pesting (a kind of distractive oxidation) of $MoSi_2$ at about 500 °C can be suppressed by the addition of Al because the volume change in the process of oxidation is largely reduced [2]. The high temperature oxidation properties of $MoSi_2$ can also be improved by the addition of Al and formation of $Mo(Si,Al)_2$ because of the formation of Al_2O_3 in the oxidation process and the restriction of the crystallization of SiO_2 which is also formed in the oxidation process [1].

Although $Mo(Si,Al)_2$ alloys have better properties than those of $MoSi_2$ alloy, few reports can be found about the details of preparing the alloys. The $Mo(Si,Al)_2$ alloys used for the study of oxidation resistance are usually prepared by the arc-melting method [1, 2]. In the present work, a $Mo(Si,Al)_2$ alloy was prepared from $MoSi_2$, Mo and Al according to the following reaction by hot pressing at low temperatures for a short time:

$$(1-x)MoSi_2 + xMo + 2xAl \longrightarrow Mo(Si_{1-x}Al_x)_2 \quad (1)$$

2. Experimental procedure

The raw powders were $MoSi_2$ (oxygen content 4.4826 wt %, measured by a TC-436 analyzer, LECO Cooperation, USA), Al powder (oxygen content 0.6758%) and Mo powder (purity 99.9%, particle size #300). In this work, only one composition was selected for investigating, that is $x = 0.40$ in $Mo(Si_{1-x}Al_x)_2$. After dry mixing $MoSi_2$, Mo and Al uniformly, the mixed powder was hot pressed in a graphite die under 20 MPa at various temperatures for various times in a vacuum. The as-received sample size was 12 diameter × 2.5 mm. After the sample surface was ground away by a diamond wheel, the density was measured by the water displacement method and the phase composition was determined by the X-ray diffraction (XRD) technique using CuK_α radiation. Then the sample was further ground by a diamond wheel into a specimen of size $2 \times 4 \times 12$ mm^3. The three-point bending strength of the material was measured on such (unpolished) bars; the outer span was 10 mm, and the crosshead speed was 0.5 mm min^{-1}. Then the surface parallel to the hot-pressing direction was polished and the Vickers hardness and fracture toughness were tested by the Vickers indentation method with an indent load of 196 N. The Evans and Charles formula [3] was adopted to calculate the fracture toughness. Scanning electron microscopy (SEM) was used to observe the microstructure of the material. Energy-dispersive X-ray analysis (EDAX) associated with scanning electron microscopy (SEM) was used to determine the phase chemistry.

3. Results and discussion

3.1. Reaction process and material microstructures

Because the theoretical densities of $Mo(Si_{1-x}Al_x)_2$ as a function of the x value are not found in the literature,

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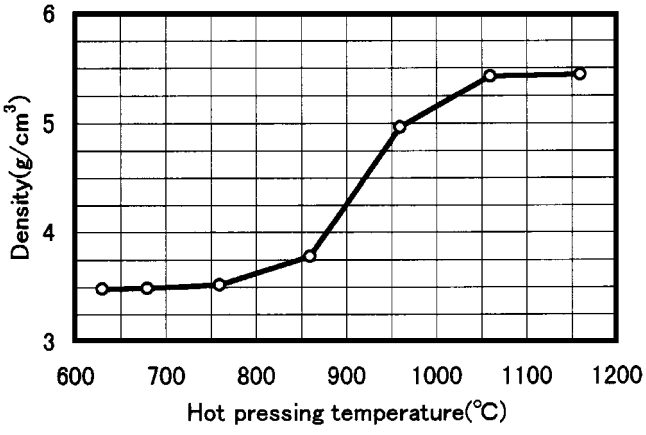


Figure 1 Effect of temperature on the density of $Mo(Si,Al)_2$ alloy from $MoSi_2$–Mo–Al prepared by hot pressing under 20 MPa for 10 min in a vacuum.

here only densities measured by the water displacement method is used (the density of $MoSi_2$ is 6.31 g cm^{-3}). Fig. 1 is the relationship between the sample density and the hot pressing temperature when hot pressing under 20 MPa for 10 min in a vacuum. It can be seen that the densification below 760 °C almost did not take place (the forming density of the sample after uniaxial pressing under 20 MPa at room temperature was about 3.1 g cm^{-3}), and above 860 °C the density increased very rapidly. When the hot pressing temperature increased to above 1060 °C the density hardly changed. Fig. 2 shows the effect of the hot-pressing time on the density of the $Mo(Si,Al)_2$ alloy when hot pressed at 1060 °C and 1160 °C respectively. It can be seen that at 1060 °C, hot pressing for shorter times than 5 min does not produce high density material, but for longer times it is possible to produce a high density alloy. However, at 1160 °C hot pressing for only 5 min can produce a high density alloy, and the density changed by very little when the soaking time was prolonged. Fig. 3 shows the XRD patterns of specimens hot pressed under various conditions. It can be seen from Fig. 3 that even at 630 °C, where aluminum does not melt (the melting point of aluminum is about 660 °C), some chemical reactions take place and a metallic component of Mo and Al is formed, but the main phases are still those of the raw mixed powder. The reaction of Equation 1 is exothermic, so the actual temperature in the center of the sample may be higher than the measured one. At 680 °C, which is a little higher than the melting point of aluminum, the main phase is changed to $Mo(Si,Al)_2$, but the crystallization of $Mo(Si,Al)_2$ formed at this temperature is not good according to the low diffraction peak intensity. Up to 860 °C the crystallization of $Mo(Si,Al)_2$ is good. This means that the fast densification of the mixed powder and the crystallization (grain growth) of the newly formed $Mo(Si,Al)_2$ takes place in the same temperature range. The reaction between $MoSi_2$, Mo and Al was accelerated with the occurrence of the aluminum melt. According to the phase diagrams of Al–Si and Al–Mo [4], at 680 °C the solubilities of silicon and molybdenum in aluminum melt are about 20 at % and less than 1 at %, respectively. So the formation of $Mo(Si,Al)_2$ in aluminum melt was controlled by the dissolution of Mo into aluminum melt. With the temperature increasing, the dissolubilities of Si and Mo in aluminum melt become larger (see Fig. 4) and thus accelerate the formation of $Mo(Si,Al)_2$.

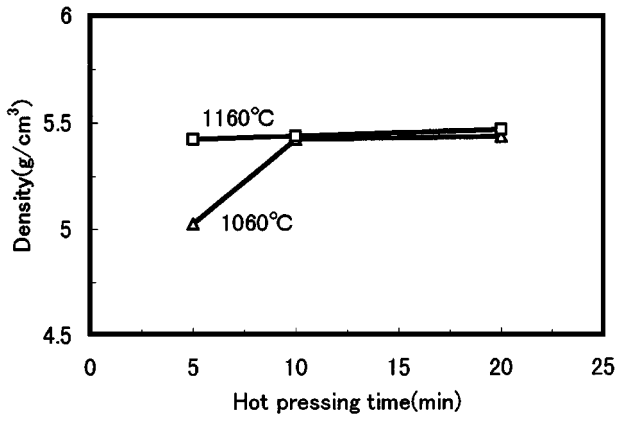


Figure 2 Effect of hot pressing time on the density of $Mo(Si,Al)_2$ alloy.

The XRD patterns of the specimens hot pressed at 1060 °C and 1160 °C for 5 min are the same as that of the specimen hot pressed at 1060 °C for 10 min, this means that the chemical reaction between $MoSi_2$, Mo and Al to form $Mo(Si,Al)_2$ at these temperatures is fast and only a very short time is needed to complete this reaction. There is no obvious peak for Al_2O_3 in the XRD patterns, but the existence of amorphous or poorly crystalized Al_2O_3 formed at such low temperatures cannot be ruled out.

Fig. 5 shows the SEM microstructures of the alloy hot pressed at 1160 °C for 20 min. The other specimens manufactured at other conditions have similar microstructures except for the specimen hot pressed at 1060 °C for 5 min, that is, there remained large pores in the microstructure and this is coincident with the measured density (Fig. 2). From Fig. 5a it can be seen that there are almost homogeneously distributed small particles (particle size about 1 μm) in the microstructure. The chemistry of these particles was examined by EDAX and the results are shown in Fig. 6. It can be seen that these particles were rich in aluminum. Such a characteristic is somewhat like that of $MoSi_2$ alloy when adding 5 wt % aluminum [5]. So it is suggested that these particles are Al_2O_3 particles in an amorphous or poor crystallization state formed at low-temperature hot pressing by the reaction of aluminum with the oxygen in the $MoSi_2$ raw powder. If all the oxygen in the $MoSi_2$ raw powder changed to Al_2O_3, the calculated content of formed Al_2O_3 is 5.55 wt %. Fig. 5b shows the fractograph of the same specimen. It shows that the particle size of $Mo(Si,Al)_2$ is generally less than 5 μm, but that there are some large particles distributed in the microstructure. The main fracture type of these alloys was intracrystalline.

3.2. Mechanical properties

Fig. 7 shows the effect of hot-pressing time on the bending strength of $Mo(Si,Al)_2$ alloys hot pressed at 1060 °C and 1160 °C. It can be seen that when hot pressed at 1060 °C the bending strength increased very

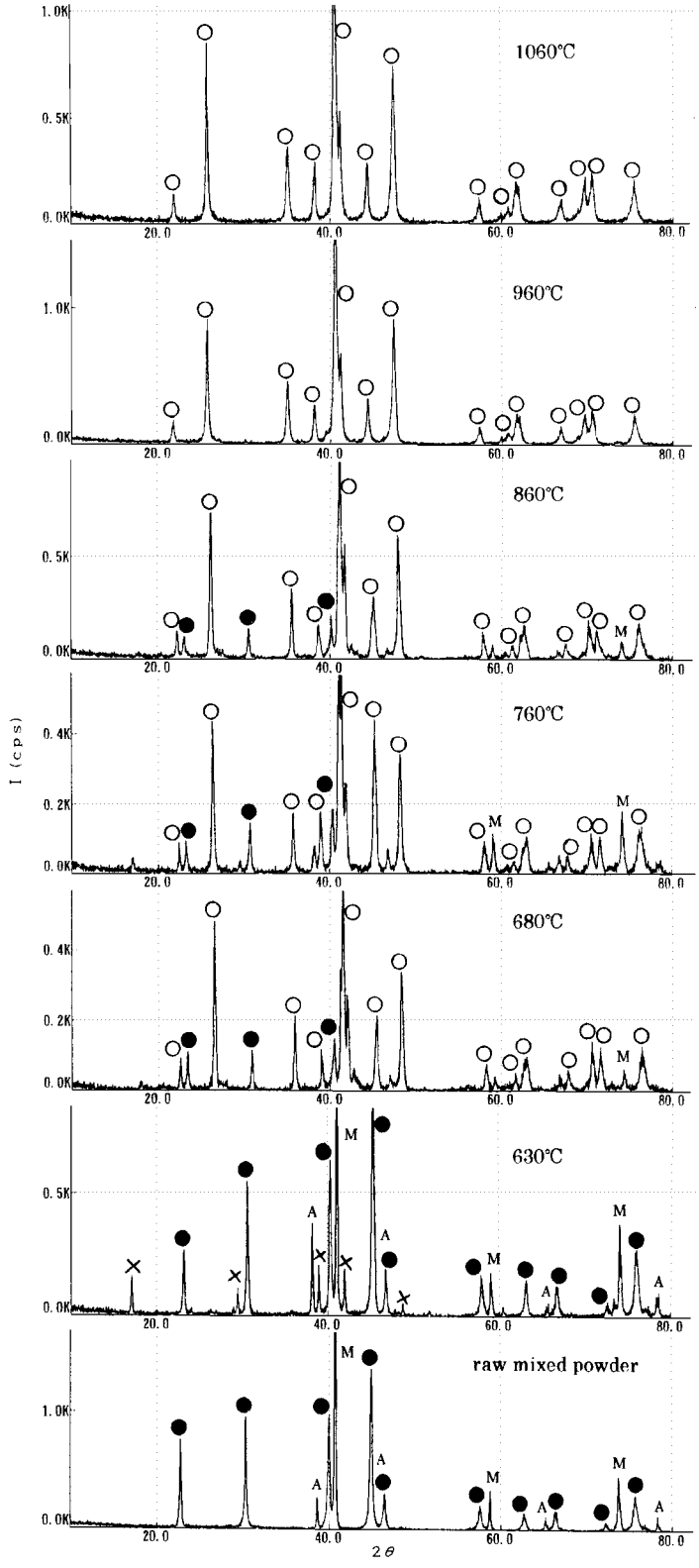


Figure 3 XRD patterns of $MoSi_2$–Mo–Al mixed powder and the specimens prepared by hot pressing at diferent temperatures for 10 min (M—Mo; A — Al; ● —$MoSi_2$; × — Mo_xAl_y; ○—$Mo(Si,Al)_2$).

rapidly when the pressing time was increased from 5 to 10 min due to the density increase. When hot pressed at 1160 °C the bending strength increased gradually from 265 MPa to 310 MPa when the pressing time was increased from 5 to 10 min. If longer pressing times such as 20 min were used, the strength would decrease gradually.

The Vickers hardness and fracture toughness of $Mo(Si,Al)_2$ alloys are shown in Figs 8 and 9. Except for the specimen hot pressed at 1060 °C for 5 min due to the low density, the other specimens have almost the same hardness. However, the toughness of the specimens hot pressed at 1060 °C and 1160 °C for 5 min had the highest values, and a longer pressing time would result in slightly lower values. It is perhaps the presence of some aluminum-based metal remaining at the grain boundaries if the soaking time was too short. Because the EDAX could not detect oxygen, it was impossible to

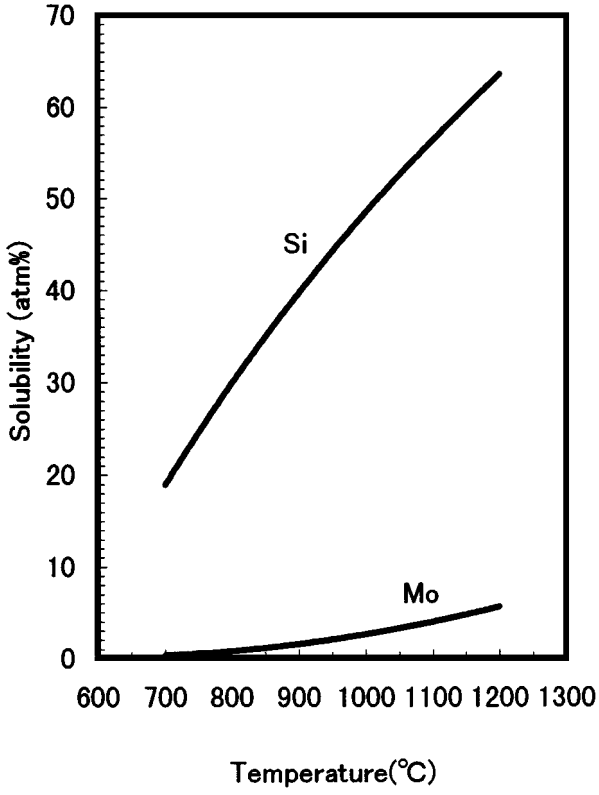
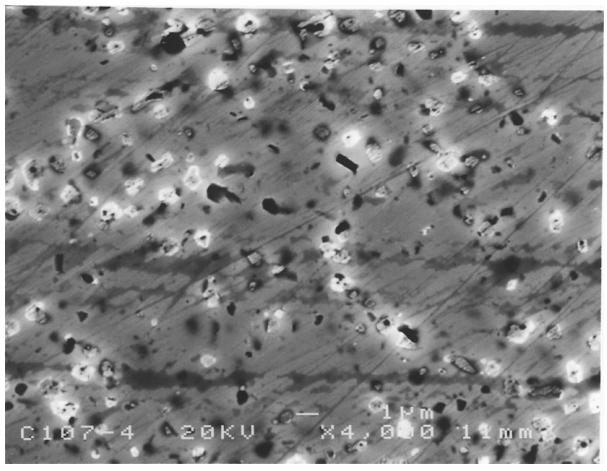
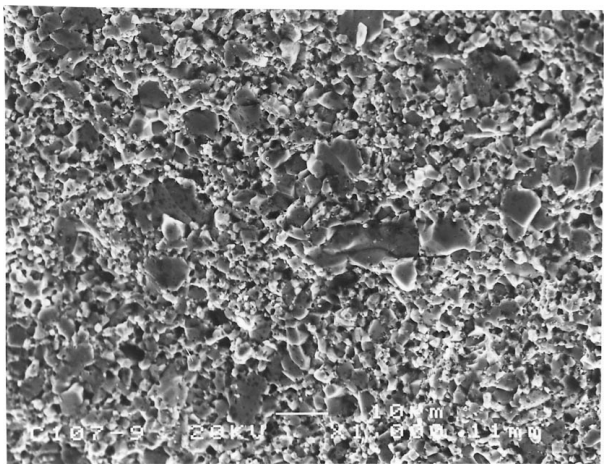


Figure 4 Solubilities of silicon and molybdenum in aluminum melt as a function of temperature.

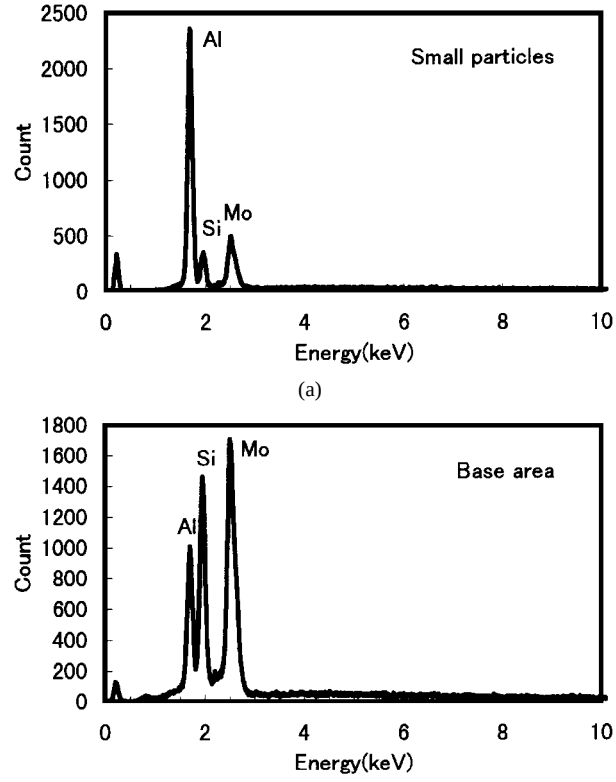


(a)



(b)

Figure 5 SEM photographs of $Mo(Si,Al)_2$ alloy hot pressed at 1160 °C for 20 min; (a) polished surface and (b) fracture surface.



(a)

(b)

Figure 6 EDAX patterns of $Mo(Si,Al)_2$ alloy prepared by hot pressing at 1160 °C for 20 min, (a) small particles, and (b) base area.

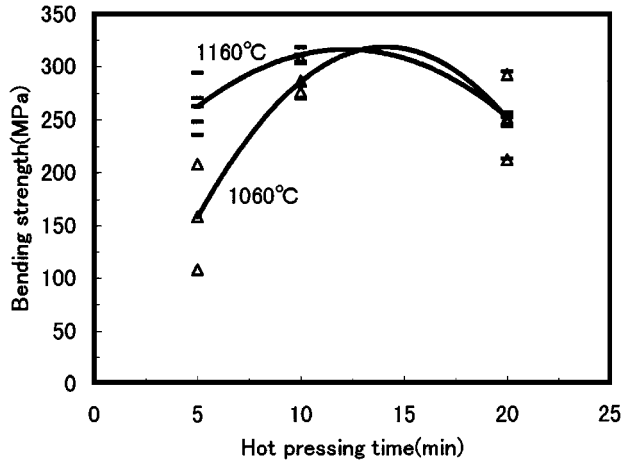


Figure 7 Effect of hot pressing time on the bending strength of $Mo(Si,Al)_2$ alloy.

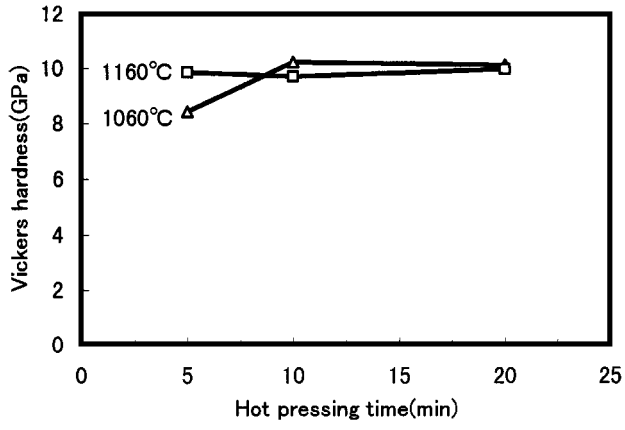


Figure 8 Effect of hot pressing time on the Vickers hardness of $Mo(Si,Al)_2$ alloy.

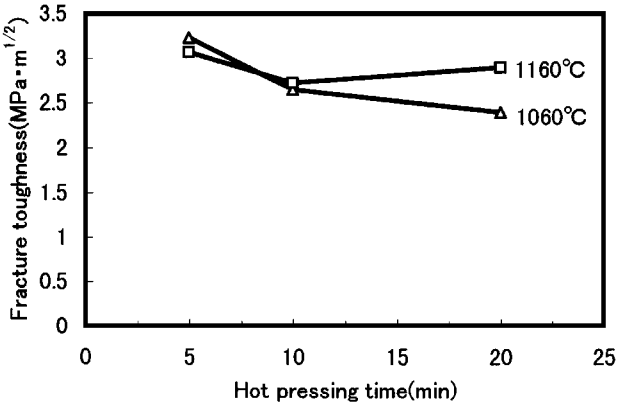
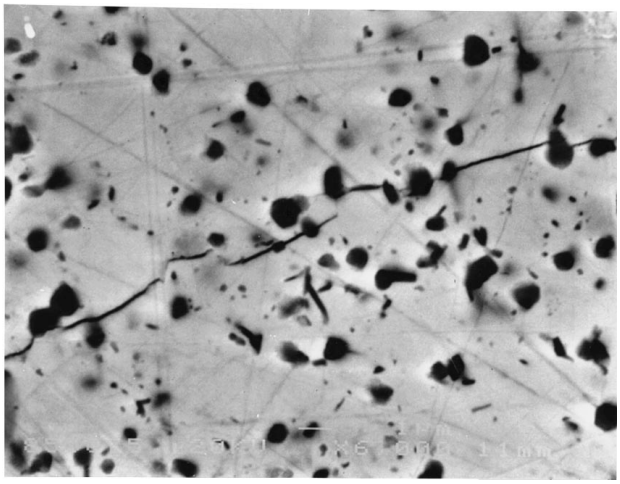
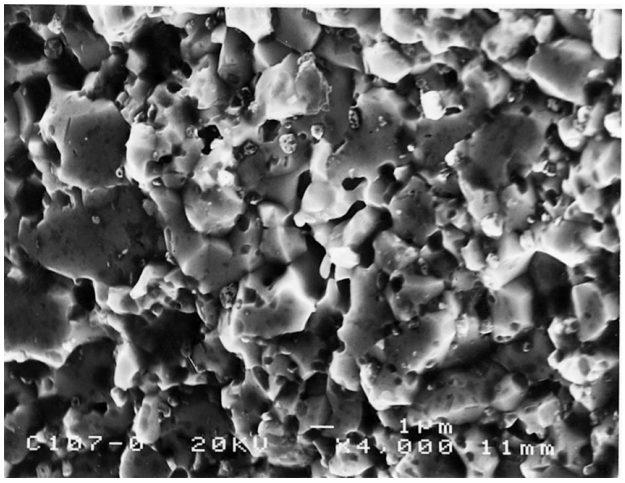


Figure 9 Effect of hot pressing time on the fracture toughness of $Mo(Si,Al)_2$ alloy.



(a)



(b)

Figure 10 Crack propagation path of $Mo(Si,Al)_2$ alloy prepared by hot pressing at 1160 °C for 20 min; (a) crack path under Vickers indentation, and (b) fracture surface showing pinning Al_2O_3 particles.

distinguish between Al_2O_3 and aluminum-based metals in the present work. Fig. 10a shows the crack propagation path under the Vickers indentation for the specimen hot pressed at 1160 °C for 20 min. It can be seen that the crack propagated discontinuously and Al_2O_3 particles generally played the role of pinning the propagating crack. These pinning Al_2O_3 particles can easily be seen in the fractograph shown in Fig. 10b. This means that Al_2O_3 particles can act as a reinforcing phase. However, the toughening and strengthening effect by crack pinning is limited when compared with other toughening mechanisms such as crack deflection by or pull-out of whiskers and platelets. On the other hand, between Al_2O_3 and $Mo(Si,Al)_2$ there are some chemical reactions at high temperatures and thus there results a strong phase interface bonding, and their thermal expansion coefficients are similar. This strong interface is somewhat beneficial to the pinning effect, but it is harmful to the crack deflection effect. Thus, it is impossible for $MoSi_2$-based alloys to get a remarkable toughening effect by adding Al_2O_3 particles.

4. Conclusions

(1) A $Mo(Si,Al)_2$ alloy was prepared by reactive hot pressing under 20 MPa at low temperatures of 1060–1160 °C for a short time of 5–20 min in a vacuum using $MoSi_2$, Mo and Al as starting powders;

(2) At 1160 °C, only 5 min of soaking time was enough to get a high density material. But at 1060 °C, 10 min was needed. The dissolution process of molybdenum into aluminum melt might be the critical one for the formation of $Mo(Si,Al)_2$. It was suggested that the oxygen present in $MoSi_2$ raw powder would react with Al to form Al_2O_3 in an amorphous or poor crystallization state;

(3) The mechanical properties of the alloys were a little higher than those of the monolithic $MoSi_2$ alloy. The Al_2O_3 particles could act as a crack-pinning element, but a large toughening effect could not be obtained by this phenomenon.

Acknowledgements

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