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Synthesis of Mo–Si–B *in situ* composites by mechanical alloying

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Abstract

In this study, the synthesis of Mo–Si–B multi-phase alloys, so-called *in situ* composites, was attempted with the combination of mechanical alloying (MA) and spark plasma sintering (SPS) processes. MA was conducted with mixed powders of Mo, Si and B using a planetary ball mill under various milling conditions. MAed powders were characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The results obtained by XRD indicated that Mo–Si–B alloyed powders were successfully produced when elemental powders were milled at a higher milling energy. Vacuum heat treatments after the MA process promoted the formation of Mo–Si–B intermetallic phase in MAed powders. MAed powders were successfully consolidated by SPS and sound compacts of Mo_5SiB_2-based composites were synthesized.

Keywords: Molybdenum silicides; Mechanical alloying; Spark plasma sintering; X-ray diffraction

1. Introduction

Mo-based composites are one of attractive materials for high temperature structural applications to achieve high energy efficiency. Especially, Mo–Si–B alloys have high potential as heat-resistant materials at ultra-high temperature [1–5]. However, the synthesis of these materials is usually difficult because of their extremely high melting temperatures. MA was developed in the 1970s for the synthesis of oxide dispersion-strengthened superalloy powders, and now is used to produce many kinds of non-equilibrium alloys, such as supersaturated solid solutions, metastable crystalline and amorphous phases and so on [6–10].

It has been demonstrated that MA is a very useful method for the synthesis of $MoSi_2$ [11,12]. While many studies on MA for the Mo–Si binary system [6–9,11–13] have been reported, the synthesis of the Mo–Si–B ternary system by MA has been hardly attempted. In this study, the synthesis of Mo–Si–B multi-phase alloys, so-called *in situ* composites, was attempted by the combination of MA and spark plasma sintering (SPS) processes.

2. Experimental procedure

Mo–Si–B mixed powders with nominal compositions of Mo/Mo_5SiB_2 (Mo–8.7 mol% Si–17.4 mol% B) and Mo_5SiB_2 (Mo–12.5 mol% Si–25 mol% B) were prepared from pure Mo (purity > 99.9%, size < 63 μm), Si (purity > 99.99%, size < 45 μm) and B (purity > 99%, size < 45 μm). Mechanical alloying was carried out with a mini planetary ball mill (Fritsch P7) at the ball-to-powder weight ratio of 5 under various milling intensities. To minimize oxidation during milling, loading into and unloading from vials were carried out inside a dry N_2-filled glove box. The mixed powders were put into a stainless steel vial together with stainless steel balls in an N_2 gas atmosphere. The ball milling rotation speed was a maximum of 500 rpm. As-mechanically alloyed powders were annealed in a vacuum at the pressure of 5×10^{-4} Pa and temperature ranging between 873 and 1873 K for 1 h. In order to fabricate dense Mo–Si–B composites, a spark plasma sintering (SPS) method was applied [14]. Starting materials were as-mechanically alloyed powders. The powders were packed into a graphite die under a compressive stress of 40 MPa, and then a pulsating current was passed in the mixed powders and through the graphite die within an chamber evacuated at 10 Pa. Sintering temperature was measured by a digital radiation thermometer, and sintering behavior was monitored by measuring change in the thickness of the compact body. The heating rate was 0.17 K/s, and the maximum sintering temperature was 1473 K. Phase and microstructural characterization of the green powders, mechanically alloyed (MAed) powders, annealed powders and products were made by scanning electron microscopy

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(SEM), X-ray diffractometry (XRD), and electron probe microanalysis (EPMA). A SEM was operated at 20 kV and equipped with an energy-dispersive X-ray (EDX) analyzer. An X-ray diffractometer was operated at 30 kV and 300 mA.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns for Mo–8.7 mol% Si–17.4 mol% B powders after mechanical alloying at the milling intensity of 200 rpm for different milling times. Sharp peaks from both Mo and Si are seen for the mixed powder before MA (Fig. 1(a)). After MA for 49 h, Si diffraction peaks are going to vanish, and Mo diffraction peaks are broadened and their intensities are lowered, as shown in Fig. 1(b). These spectra indicate that no chemical reaction between Mo, Si and B occurs during the ball milling process. When MA duration is increased to 100 h (Fig. 1(c)), Si diffraction peaks completely disappear. Mo diffraction peaks are further broadened and their intensities lowered. No new diffraction peaks are observed at this milling condition.

One aim of this study is to synthesize Mo/Mo_5SiB_2 *in situ* composite. Therefore, vacuum annealing were performed for the MAed mixed powder to obtain the Mo/Mo_5SiB_2 *in situ* composite powder. Fig. 2 shows X-ray diffraction patterns of MAed Mo–8.7 mol% Si–17.4 mol% B mixed powder after a vacuum heat treatment for 1 h at temperature ranging between 873 and 1873 K. The peaks from Mo reflection ($2\theta = 40.516^\circ$, 58.609° and 73.684°) become sharper in comparison with as-MAed powder (Fig. 1(c)). As shown in Fig. 2(a) and (b), sharp peaks from Mo are clear and no diffraction peak from Mo–Si–B compound is observed. An increase in heat treatment temperature 1073–1273 K leads to the appearance of new diffraction peaks with no Mo peak (Fig. 2(c)). A small amount of Mo_2B is formed after the heat treatment in the MAed powder. With further increasing heat treatment temperature (Fig. 2(d)–(f)), the peaks from Mo_2B reflection become sharper and larger, indicating an increase in the amount of Mo_2B. From the above results, it is concluded that the formation of Mo–Si–B alloy phase is not promoted even by the vacuum heat treatments probably because of a stronger reactivity between Mo and B.

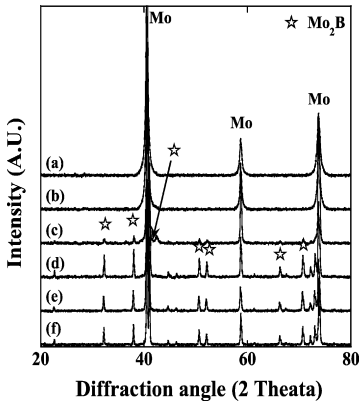

Fig. 2. X-ray diffraction patterns of MAed Mo–8.7 mol% Si–17.4 mol% B mixed powder (200 rpm, 100 h) annealed at various temperatures: (a) 873 K; (b) 1073 K; (c) 1273 K; (d) 1473 K; (e) 1673 K; (f) 1873 K.

In order to promote the synthesis of Mo–Si–B *in situ* compounds, alloying behavior by MA with higher energy was investigated. The XRD results of Mo–8.7 mol% Si–17.4 mol% B mixed powder after milling for 100 h in the planetary mill under various milling intensities of (a)–(d) are shown in Fig. 3. It is indicated that the intensity of Mo peaks gradually decreases as the milling energy increases. Further increase in milling energy caused the broadening of Mo diffraction peaks. The peak broadening should be due to grain size refinement, amorphous phase formation plus the introduction of internal strain. As seen in this figure, the background intensity (especially condition (d)), in the angle range of $2\theta = 39$–45°; is increased with increas-

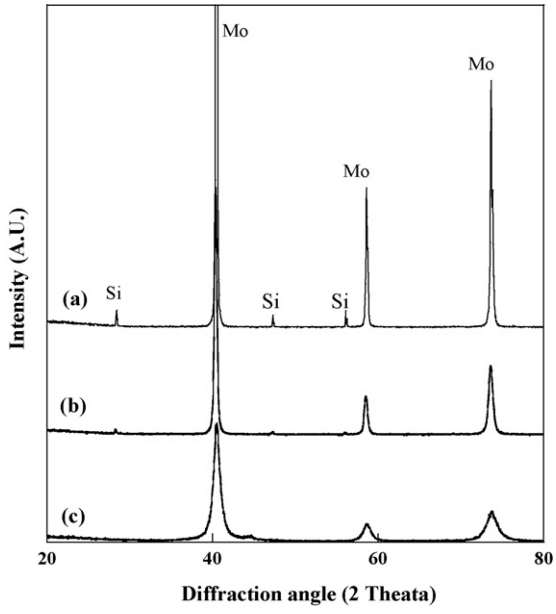

Fig. 1. X-ray diffraction patterns of Mo–8.7 mol% Si–17.4 mol% B mixed powder milled at 200 rpm for various times: (a) as-mixed; (b) 49 h; (c) 100 h.

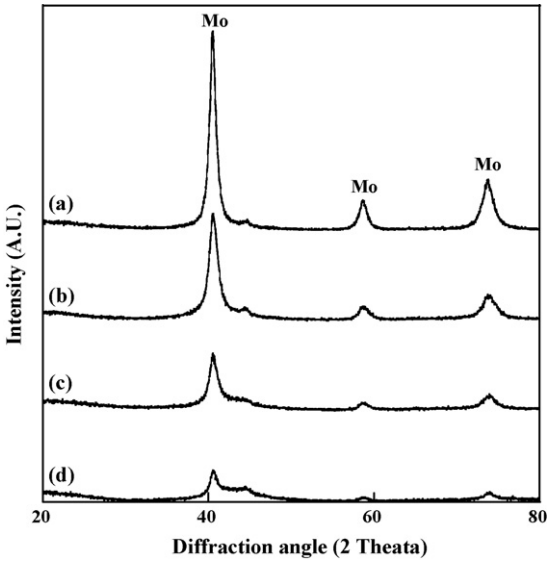

Fig. 3. X-ray diffraction patterns of Mo–8.7 mol% Si–17.4 mol% B mixed powder milled for 100 h at various milling intensities: (a) 200 rpm; (b) 300 rpm; (c) 400 rpm; (d) 500 rpm.

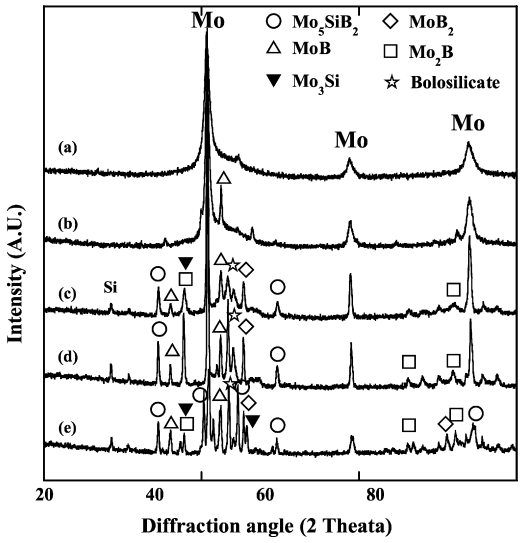

Fig. 4. X-ray diffraction patterns of MAed Mo–8.7 mol% Si–17.4 mol% B mixed powder (500 rpm, 100 h) annealed at: (a) 873 K; (b) 1073 K; (c) 1273 K; (d) 1473 K; (e) 1673 K.

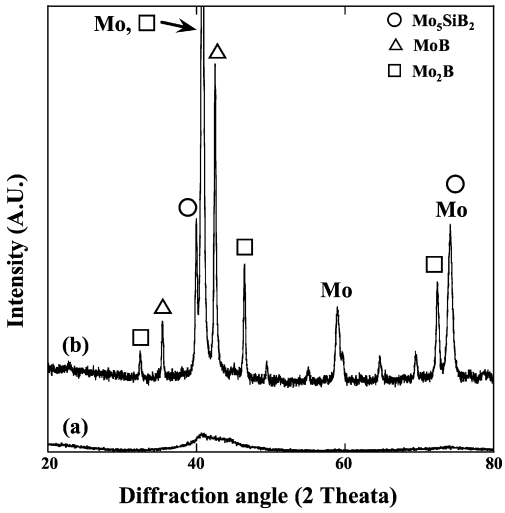

Fig. 5. X-ray diffraction patterns of Mo–12.5 mol% Si–25 mol% B mixed powder milled at 500 rpm for 100 h (a) and annealed at 1073 K (b).

ing milling energy. This suggests that, after MA of 500 rpm, the mixed powder may consist of amorphous and/or nanocrystalline phases. MA with high energy may cause phase transitions in Mo–8.7 mol% Si–17.4 mol% B mixed powder.

All the MAed mixed powders were annealed in a vacuum furnace with the same heat treatment condition as described above. Fig. 4 shows XRD patterns of the Mo–8.7 mol% Si–17.4 mol% B powder MAed at 500 rpm for 100 h and annealed at various temperatures (873–1673 K). The diffraction pattern after annealing at 873 K is almost identical to that of the as-MAed powder. As shown in Fig. 4(a), a diffuse amorphous halo peak is seen, indicating almost no reaction occurs up to 873 K. After annealing at 1073 K, peaks from MoB are shown up. After annealing at 1273 K and above, more peaks from the compounds such as Mo_5SiB_2, Mo_2B, MoB_2, Mo_3Si, Si are observed, as shown in Fig. 4(c)–(e). These results indicate that the reactions in the milled Mo–8.7 mol% Si–17.4 mol% B mixed powder are enhanced by increasing annealing temperature. Moreover, the position of Mo peak ($2\theta = 40.516°$) is shifted to higher diffraction angles with increasing annealing temperature. Formation of Mo_2B phase ($2\theta = 41.011°$) increases.

In order to synthesize Mo_5SiB_2 powder, Mo–12.5 mol% Si–25 mol% B mixed powder was also mechanically alloyed at 500 rpm for 100 h. Fig. 5 shows X-ray diffraction patterns of as-MAed (a) and annealed (b) powders. After ball milling at 500 rpm for about 100 h, considerably broadened peaks from Mo solid solution were detected in the XRD pattern (Fig. 5(a)). On the other hand, the diffraction pattern after the ball milling followed by annealing at 1073 K shows Mo, Mo_5SiB_2, MoB and Mo_2B, as shown in Fig. 5(b). Consequently, the direct synthesis of Mo–Si–B *in situ* composite powder (Mo and Mo_5SiB_2) was unsuccessful by MA and heat treatment.

According to the above results, MA process should be improved for the synthesis of Mo–Si–B *in situ* composites. MA is a solid state processing technique through repeated fracturing and cold welding of powder particles in a dry high-energy ball mill. Particle welding leads to the formation of a composite layer structure. Thus, MA process was used to progress step-by-step for the synthesis of Mo–Si–B *in situ* composites in this study. The first step is to mechanically alloy the mixed powder of Mo and Si at 500 rpm for 50 h. The second step is to mechanically alloy the above mixed powder with B at 500 rpm for 50 h. MAed time is totally 100 h until the second step. Finally the MAed mixed powder was sintered at 1473 K and 40 MPa by SPS. Pol-

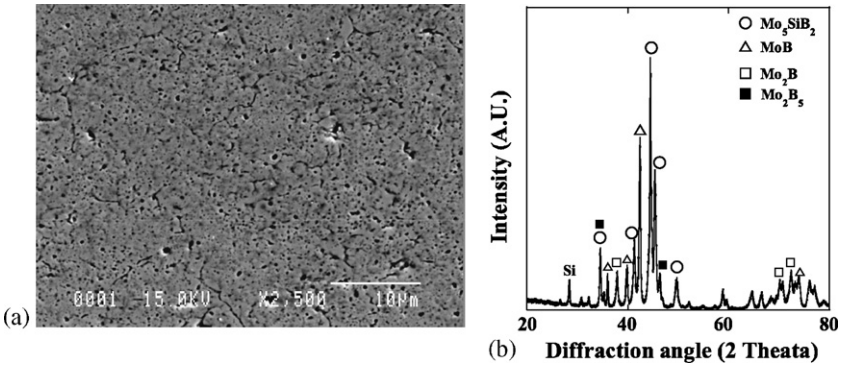

Fig. 6. SEM micrograph (a) and X-ray diffraction pattern (b) of the sintered Mo–12.5 mol% Si–25 mol% B mixed powder.

ished surface of the Mo–12.5 mol% Si–25 mol% B compact was observed by SEM. Fig. 6 shows a SEM image and XRD pattern of Mo–12.5 mol% Si–25 mol% B sintered compact. As shown in Fig. 6(a), it is seen that the compact is relatively dense. SiO_2 inclusions, which may be formed with adsorbed oxygen, are clearly observed. From the result of Fig. 6(b), the gray matrix contains Mo_5SiB_2, MoB, Mo_2B and Mo_2B_5. Moreover, quantitative analysis of the sintered compact by EPMA shows that the matrix has almost the Mo_5SiB_2 composition. Therefore, the MA and SPS combined process is one of useful ways to synthesizes Mo_5SiB_2-based composites.

4. Conclusions

In this study, Mo_5SiB_2 was successfully obtained from Mo–12.5 mol% Si–25% B mixed powder by mechanical alloying and spark plasma sintering, whereas Mo–8.7 mol% Si–17.4 mol% B mixed powder was not entirely converted to Mo/Mo_5SiB_2 *in situ* composites. Since the reaction between Mo and B is preferred, Mo–Si compounds formation could be suppressed in MA processes.

Acknowledgments

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