Thermal stability and decomposition paths of MoAlB ceramic

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ABSTRACT
The thermal stability of MoAlB powder was studied. The effects of vacuum, Ar protection, molten salt treatment, and additives (B and C) on its thermal stability were studied. Results showed that MoAlB powder would react with a small amount of O2 in the furnace under vacuum and low temperature to form MoB, Al2Mo, B2O3, and Al2O3. At higher temperature, MoAlB first decomposed into MoB and Al. Al was oxidized to Al2O3. The thermal stability of MoAlB powder was better under the protection of Ar. However, molten salt heat treatment and additives such as B and C could promote the decomposition of MoAlB.

1. Introduction
The chemical bonds in the crystal structure of MAB phase material [1] (M is a transition metal, A is a group IIIA or IVA element, and B is B element) show obvious anisotropy. M–B is a strong covalent bond, while M–A is a weak bond. This kind of chemical bond characteristic enables them to combine the common advantages of metal and ceramic [2,3], including high-temperature resistance, oxidation resistance, thermal shock resistance, electrical conductivity, heat conduction, non-brittleness, and easy processing. MoAlB is a typical representative of MAB phase, which has been widely studied due to its excellent electrical and thermal conductivity, good fracture toughness, excellent high-temperature oxidation resistance, and crack self–healing characteristics [4-7].

Studying the high-temperature thermal stability of MoAlB as a potential high-temperature structural material is important. Some studies have reported the thermal stability of Mn2AlB3 [8], MoAlB [9], and Fe2AlB2 [10,11] in protective or vacuum atmosphere. The results showed that their bulk materials are stable at 1380, 1708, and 1440 K, respectively. If the temperature continues to increase, then the corresponding binary borides (MnB, MoB, or FeB) and Al will be obtained by the decomposition of these MAB phases.

Al atoms in the MAB phase diffuse outward at high temperature; therefore, the bonding strength of Al–B and M–Al bonds is obviously weaker than that of B–B and M–B bonds [12,13]. The thermal stability of MoAlB in MoAlB–Al system was studied in references [14,15]. The results showed that MoAlB can react with Al to form Al2Mo and a small amount of AlB2 and MoB2. The formation of Al2Mo inhibits the diffusion of Al atoms, and this condition hinders the decomposition reaction of MoAlB.

Research on high-temperature thermal stability of MoAlB ceramics is insufficiently comprehensive, and only the abovementioned related research [9,14,15] are available. Although MoAlB bulk exhibits good thermal stability, little is known about its phase transition path. In practical high-temperature applications, MoAlB materials often need to be in a specific atmosphere (vacuum or Ar protection), corrosive environment (such as molten salt), or composite with other materials (such as carbon materials).

This study aimed to investigate the effects of protective atmosphere (vacuum and argon), molten salt, and additives (B or carbon) on the thermal stability of MoAlB materials.

2. Experimental procedure
MoAlB powder (approximately 53 μm, 99.0% purity) was purchased from Laizhou Kai Ceramic Materials Co., Ltd. B (2 μm in average, 99.0% purity) was purchased from Dandong Chemical (Shanghai) Co., Ltd. Anhydrous NaCl and KCl (analytical purity) were purchased from Tianjin Zhiyuan Chemical Plant Co., Ltd. Carbon black (30 nm in average) was purchased from Daosheng Chemical (Shanghai) Co., Ltd.

NaCl and KCl were mixed in the same ratio and then mixed with MoAlB powder in the mass ratio of 2:1. B or C and MoAlB were proportioned according to the molar ratio of the same substance. The abovementioned powder was mixed by hand in a mortar for 1 h to ensure homogeneity. The single-phase powder was placed in a crucible and then placed into a vacuum...
carbon tube furnace. Vacuum (vacuum degree of nearly $10^{-2}$ Pa) heat treatment was conducted at different temperatures. The heating rate was 10°C/min, the holding time was 1 h, and the cooling was furnace cooling. The single-phase powder, other salt-containing powder, and additive-containing mixed powder were placed into the crucible first and then placed into the tubular furnace. Under the protection of Ar, the heating and cooling rates were 10°C/min and the holding time was 1 h. After heat treatment, the salt-containing powders should be washed and dried before characterization.

The heat-treated products were characterized by X-ray diffraction (XRD, D/MAX-2500PC) and field-emission scanning electron microscopy (FE-SEM, Quanta 250 FEG).

![Figure 1](image1.png)

**Figure 1.** XRD patterns of single phase MoAlB powders by vacuum heat treatment at different temperature for 1 h.

![Figure 2](image2.png)

**Figure 2.** XRD patterns of single phase MoAlB, B/MoAlB and C/MoAlB powders by heat treatment at 1373 K for 1 h under Ar protection.
3. Results and discussion

Figure 1 shows the XRD patterns of samples obtained by vacuum heat treatment at different temperatures for 1 h. As shown in the figure, a small amount of MoAlB was decomposed to MoB and Al₃Mo at 1073–1273 K. However, when the temperature further rose up to 1373 K, MoAlB was completely decomposed into MoB. Weak peaks of Al₂O₃ were observed in the samples at all temperatures, which might be due to the oxidation of MoAlB or Al obtained by the decomposition products of MoAlB.

Figure 2 shows the XRD of single-phase MoAlB, B/MoAlB, and C/MoAlB mixed powder by heat treatment under the protection of Ar at 1373 K for 1 h. Figure 2(a) shows that the thermal stability of single-phase MoAlB was much better than that of vacuum-treated samples (Figure 1). Only a small amount of MoAlB was decomposed into Al₃Mo and MoB. However, adding B or C led to the complete decomposition of MoAlB (Figure 2(b, c)). The heat treatment products of B/MoAlB mixed powders were composed of MoB, MoB₂, MoB₂.₅, and Al₂O₃. Obviously, B reacted with MoAlB to form MoB₂ or MoB₂.₅. The heat treatment products of C/MoAlB mixed powders were composed of MoB and Al₂O₃.

Figure 3 shows the SEM image of single-phase MoAlB, B/MoAlB, and C/MoAlB mixed powders by heat treatment under the protection of Ar at 1373 K for 1 h. As shown in Figure 3(a), MoAlB powder was still loose and mainly composed of micron-scale particles. Many nanoparticles adhered to the surface of MoAlB, and they were probably Al₃Mo and MoB particles according to the XRD results. Figure 3(b) shows that the grains in the sample obtained from B/MoAlB powders had a different size of nanometer to micron scale. Figure 3(c) shows that the MoB grain size of C–MoAlB sample was nearly 50–100 nm.

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**Figure 3.** SEM images of MoAlB, B/MoAlB and C/MoAlB powders by heat treatment at 1373 K for 1 h under Ar protection.
Figure 4. XRD patterns of MoAlB, B/MoAlB and C/MoAlB powders by molten salt heat treatment at 1373 K for 1 h under Ar protection.

Figure 4 shows the XRD pattern of single-phase MoAlB, B/MoAlB, and C/MoAlB mixed powder by molten salt heat treatment under the protection of Ar at 1373 K for 1 h. Figure 4(a) reveals that MoAlB powder was completely decomposed to form MoB and AlMo3. The weak diffraction peak of Al2O3 indicated a trace of Al2O3 in the product. The B–MoAlB product in Figure 4(b) was quite different from that of heat treatment without molten salt (Figure 2(b)). The product was composed of MoB2.5, Al2O3, Al, MoAlB, and AlB2 materials. The XRD pattern of the products from C–MoAlB mixed powder showed MoB and Al2O3, which were the same as those of the heat-treated products without molten salt (Figure 2).

Figure 5 shows the SEM image of MoAlB (a–b), B/MoAlB (c–d), and C/MoAlB (e–f) mixed powder by molten salt heat treatment at 1373 K under the protection of argon. The low-amplification SEM images (Figure 5(a,c,e)) indicate that the sample was composed of many larger particles with a hairy surface. The high-amplification SEM images (Figure 5(b,d,f)) reveal that the sample was composed of dense flower-like structure with a large number of nanosheets. The element area scanned by EDS in Figure 6 indicates that these nanosheets were Al2O3.

Figure 7 shows the XRD and SEM images of the MoAlB powder obtained by molten salt heat treatment corroded by NaOH solution. Al2O3 was removed. As shown in Figure 7(a), the product consisted of a large amount of MoB, Al3Mo, and MoAlB.

The results showed that the Al2O3 layer fully encapsulated the surface of MoB, Al3Mo, and MoAlB grains.

This phenomenon affected the detection of MoAlB by X-ray, which resulted in the absence of MoAlB peaks in Figure 4(a). Figure 7(b) shows that the sample was composed of a large number of MoB grains, which was similar to the result in Figure 3.

Figures 4–7 fully show that the decomposition reaction of single-phase MoAlB powder produced MoB and Al. Al element was also precipitated outward from MoAlB decomposition zone with the help of molten salt, and it then oxidized to Al2O3. Finally, molten salt promoted the oriented growth of Al2O3 grains and developed into nanosheets, which surrounded the surface of MoB and MoAlB grains.

The abovementioned research indicates that vacuum, argon protection, additives, and molten salt environment greatly influenced the high-temperature thermal stability of MoAlB powders. We calculated the Gibbs free energy (ΔG) values of the following chemical reactions at different temperatures using the thermodynamic data of Mo-Al-B system provided in references [9,16,17], as shown in Figure 8. On the basis of the previous works [9,14,15] and the experimental and thermodynamic results of this study, we analyzed the influence mechanism of these factors on the decomposition of MoAlB.

(1) Effect of vacuum, argon protective atmosphere, and molten salt environment

The decomposition mechanism of MoAlB can be simplified as the following Equation (9).
Figure 8 shows that the $\Delta G$ values of the decomposition reaction (1) of MoAlB were positive and below 1800 K. Obviously, MoAlB material was stable before this temperature. The results of reference [9] showed that MoAlB was stable at 1708 K. The result [9] was also consistent with the thermodynamic finding of the present study.

However, a trace of $O_2$ will always be present in the environmental system. Thus, MoAlB may react with $O_2$ as follows (2) and (3).

$$\text{MoAlB} + 0.75O_2 = \text{MoB} + 0.5\text{Al}_2\text{O}_3$$  \hspace{1cm} (2)

$$\text{MoAlB} + 0.5O_2 = (5/6)\text{MoB} + (1/6)\text{Al}_3\text{Mo} + 0.25\text{Al}_2\text{O}_3 + (1/12)\text{B}_2\text{O}_3$$  \hspace{1cm} (3)

The $\Delta G$ values of reactions (2) and (3) were relatively negative, which indicated that both reactions were prone to occur.

No $\text{B}_2\text{O}_3$ was observed in the XRD patterns of the reaction products (Figures 1 and 2), which might be due to that $\text{B}_2\text{O}_3$ easily evaporated into the environment. A similar phenomenon has been reported and discussed in detail in many studies [4,5,7] on the oxidation of MoAlB.

MoAlB powder was in protective atmosphere or vacuum. Thus, the oxygen content in the environment was very small. At the same time, the formed $\text{Al}_3\text{Mo}$ and $\text{Al}_2\text{O}_3$ could act as a protective layer, which avoided the further entry of $O_2$ and oxidation of MoAlB materials.

Notably, the MoAlB powder used in this study was in powder state, and its specific surface area was much larger than that of bulk. Therefore, it acted as a protective layer and began to oxidize below 1273 K in this study; this result did not contradict the fact that MoAlB bulk has excellent high-temperature oxidation resistance [4,5,7].
Figure 1 shows that vacuum could significantly promote the decomposition of MoAlB, and its decomposition temperature dropped sharply from 1708 K to 1373 K. Reference [9] inferred that the sublimation of Al might lead to the decrease in the thermal stability of MoAlB in vacuum. Literature [18] pointed that the vacuum degree greatly influenced the evaporation temperature of Al. At atmospheric pressure, Al must be heated to 2673 K to evaporate. However, a large amount of Al could evaporate as long as it was heated to 1269 K at vacuum degree of 10^{-2} Pa (in this experiment). When the temperature was below 1269 K, Al could not evaporate into the environment in this experiment. When the temperature reached 1269 K and above, Al began to evaporate. If the temperature would continue to rise to 1100 °C, then MoAlB would be completely decomposed into MoB and Al. A large amount of Al could rapidly evaporate into the environment. As a result, Al could not react with MoAlB sufficiently to form Al_{2}O_{3}. Therefore, the main phase of the final product was MoB, and a small amount of Al_{2}O_{3} existed.

\[ \text{MoAlB} = \text{Mo}_{7}\text{Al}_{6}\text{B}_{7} + \text{Al} \quad (4) \]

\[ \text{Mo}_{7}\text{Al}_{6}\text{B}_{7} = 7\text{MoB} + 6\text{Al} \quad (5) \]

\[ 4\text{Al} + 3\text{O}_2 = 2\text{Al}_{2}\text{O}_3 \quad (6) \]

From the abovementioned analysis, we could speculate the decomposition mechanism of MoAlB in vacuum. When the temperature was lower than the evaporation temperature of Al, MoAlB would react with trace O_2 in the furnace to form MoB, Al_{3}Mo, and Al_{2}O_{3}. When the temperature reached evaporation temperature and above, MoAlB first transformed into Mo_{7}Al_{6}B_{7} and Al. Then, Mo_{7}Al_{6}B_{7} rapidly decomposed into MoB and Al. Amounts of Al escaped from the product, and small amounts of Al reacted with O_2 to form Al_{2}O_{3}.

Therefore, the decomposition process of MoAlB powders under vacuum was a low-temperature
oxidation and high-temperature decomposition. The vacuum degree obviously affected the evaporation temperature of Al and played a key role in the decomposition process of MoAlB.

The abovementioned decomposition mechanism can fully explain the decomposition of MoAlB powder under Ar protection or molten salt environment. The decomposition mechanism of MoAlB under Ar atmosphere was similar to that of lower temperature (below 1269 K) under vacuum. Therefore, the decomposition of MoAlB under the protection of Ar was not serious. This phenomenon can fully explain the results of Figure 2(a) and literature [9].

The molten salt environment can effectively protect the powder to avoid invasion of oxygen. Molten salt can promote the migration of Al out of MoAlB decomposition region and accumulation on the surface of MoAlB crystal. Then, Al was oxidized to form Al₂O₃. Al₂O₃ crystals will grow into nanosheets under the action of molten salt. Finally, the surface of MoB products will be coated with Al₂O₃ nanoflowers (Figure 5).

(1) Influence of B additive

The XRD results in Figure 2 confirm that B reacted with MoAlB to form MoB₂ or MoB₂.5. AlB₂ could be formed by the reaction of Al and B. Strong MoB peaks also existed, which indicated that B could also act as a catalyst to promote the decomposition of MoAlB. The possible reactions are as follows:

![Figure 7. (a)XRD patterns and (b)SEM images of MoAlB obtained by molten salt heat treatment and subsequently NaOH washing.](image-url)
Notably, the molten salt environment greatly influenced the phase composition of the products after heat treatment. In the absence of molten salt, a small amount of MoB2 and MoB were observed. At the same time, the diffraction peak of Al2O3 was stronger. However, Al and AlB2 by-products could be observed in the molten salt B–MoAlB product. At the same time, the diffraction peak of Al2O3 was much weaker. Molten salt environment could effectively protect the powder and prevent the invasion of oxygen. Thus, a large amount of Al in the product could be avoided oxidation. At the same time, part of Al could react with B to form AlB2. Accordingly, a certain amount of Al and AlB2 were observed in molten salt products. In addition, the molten salt was helpful to the diffusion of B, which resulted in overcoming the barriers of MoB2 formation. B element easily migrated to the unreacted MoAlB grains, fully reacted with them, and transformed into MoB2.5.

(1) Influence of C additive

The abovementioned XRD results reveal that C could induce MoAlB to decompose and form MoB and Al after heat treatment (regardless of the presence of molten salt). Then, Al reacted with O to form Al2O3. However, C or possible carbonaceous compound (Al6C3) could not be observed in the product, which might be due to its high reaction activity, which reacted with oxygen in the environment to produce CO2 and was consumed. The abovementioned research shows that C played one catalyst effect on the decomposition of MoAlB. The specific principle should be further studied in the future.

4. Conclusion

The thermal stability of MoAlB powder was studied. The decomposition process of MoAlB powders under vacuum was a low-temperature oxidation and subsequent high-temperature decomposition. At higher temperature, MoAlB decomposed directly into MoB and Al. Al was oxidized to Al2O3. The thermal decomposition mechanism of MoAlB powder under Ar protection and molten salt heat treatment was similar to that of MoAlB powder at lower temperature under vacuum. B could induce the complete decomposition of MoAlB at low temperature and form boron-rich molybdenum compounds, such as MoB2 and MoB2.5. C could induce MoAlB to decompose into MoB and Al2O3.

Disclosure statement

The authors declare that they have no competing interests.

Funding

This project was sponsored by the National Natural Science Foundation of China (51864028 51973246, 51805557). Key scientific and technological projects in Henan Province (J12102210465), Natural Science Foundation of Henan [202300410513], Innovation and entrepreneurship training plan for Provincial College Students in Henan Province (S202010465023), Program for Interdisciplinary Direction Team in Zhongyuan University of Technology, Program for
Science and Technology Innovation Talents in Universities of Henan Province (19HASTIT024), National Natural Science Foundation of China [U2030207].

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