Comparison of Structure and Properties of Mo$_2$FeB$_2$-Based Cermets Prepared by Welding Metallurgy and Vacuum Sintering

Hu Xu, Junsheng Sun *, Jun Jin, Jijun Song and Chi Wang

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, Shandong, China; xh0714@mail.sdu.edu.cn (H.X.); 201733689@mail.sdu.edu.cn (J.J.); 200799013860@mail.sdu.edu.cn (J.S.); Q1817209090@163.com (C.W.)

Abstract: At present, most Mo$_2$FeB$_2$-based cermets are prepared by vacuum sintering. However, vacuum sintering is only suitable for ordinary cylinder and cuboid workpieces, and it is difficult to apply to large curved surface and large size workpieces. Therefore, in order to improve the flexibility of preparing Mo$_2$FeB$_2$ cermets, a flux cored wire with 70% filling rate, 304 stainless steel, 60 wt.% Mo powder and 40 wt.% FeB powder was prepared. Mo$_2$FeB$_2$ cermets were prepared by an arc cladding welding metallurgy method with flux cored wire. In this paper, the microstructure, phase evolution, hardness, wear resistance and corrosion resistance of Mo$_2$FeB$_2$ cermets prepared by the vacuum sintering (VM-Mo$_2$FeB$_2$) and arc cladding welding metallurgy method (WM-Mo$_2$FeB$_2$) were systematically studied. The results show that VM-Mo$_2$FeB$_2$ is composed of Mo$_2$FeB$_2$ and γ-CrFeNi. WM-Mo$_2$FeB$_2$ is composed of Mo$_2$FeB$_2$, NiCrFe, MoCrFe and CrB$_3$. The volume fraction of hard phase in WM-Mo$_2$FeB$_2$ is lower than that of VM-Mo$_2$FeB$_2$, and its hardness and corrosion resistance are also slightly lower than that of VM-Mo$_2$FeB$_2$, but there are obvious pores in the microstructure of VM-Mo$_2$FeB$_2$, which affects its properties. The results show that WM-Mo$_2$FeB$_2$ has good diffusion and metallurgical bonding with the matrix and has no obvious pores. The microstructure is compact and the wear resistance is better than that of VM-Mo$_2$FeB$_2$.

Keywords: VM-Mo$_2$FeB$_2$; WM-Mo$_2$FeB$_2$; phase evolution; wear resistance; corrosion behavior

1. Introduction

With its high hardness, high melting point, good wear resistance and corrosion resistance, metal borides are often widely used in mechanical processing, ore grinding, alloy smelting, parts manufacturing and other fields [1–4]. In the past few years, remarkable achievements have been made in the study of the structures and properties of different types of metal borides, such as the top-down nanostructures of Strontium Hexaboride [5], the phase stability in ternary (Ba$_3$Ca$_{1-x}$)$_2$B$_6$ and (Ba$_3$Sr$_{1-x}$)$_2$B$_6$ compounds [6], and the anisotropic thermal expansion properties of MoAlB$_2$, Cr$_2$AlB$_2$, Mn$_2$AlB$_3$ and Fe$_2$AlB$_2$ of selective layered ternary transition metal borides [7]. These ternary boride-based technical ceramics have great potential to replace cemented carbide materials. In particular, Mo$_2$FeB$_2$ based cermets show superior mechanical properties and economic benefits than other cermets, and have attracted extensive attention compared with other cermets [8–10].

The Mo$_2$FeB$_2$ hard phase is formed by in situ boriding reaction without separate preparation using vacuum liquid phase sintering technology [11,12], which overcomes the disadvantages of poor sinterability and difficulty reacts with binder metal to form brittle
phase compared with traditional sintering process. Yu et al. [13] fabricated Mo$_2$FeB$_2$ based cermets using vacuum sintering at different temperatures with different holding time and revealed that the increase of sintering temperature or holding time promoted the development of elongated Mo$_2$FeB$_2$ grains when the sintering temperature was below 1250 °C. In addition, further studies showed that the contents of alloying elements significantly decreased the grain size [14,15]. Li et al. [16] added WC in Mo-Fe-B-Cr-Ni system carrying out the vacuum sintering to form the Mo$_2$FeB$_2$-WC double hard phases, which improved the bending strength and hardness of the material.

At present, the vacuum liquid phase sintering method is mostly used to prepare Mo$_2$FeB$_2$ based ceramics, but this method is only limited to ordinary cylinders and cuboids, and the flexibility is not enough, so it is relatively difficult to prepare large curved surface and large-size workpieces. Argon arc welding has achieved good results in the preparation of such workpieces [17–19]. Therefore, in order to improve its flexibility, flux cored wire can be prepared and Mo$_2$FeB$_2$ cermet can be prepared on the surface of workpiece by argon arc welding metallurgy. This method can be applied to any curved surface of any shape and can also produce a large area of workpiece surface, which greatly improves its application range.

2. Materials and Methods

The material used for preparing Mo$_2$FeB$_2$-based cermets by an arc cladding welding metallurgical method (WM-Mo$_2$FeB$_2$) is flux cored wire, and the technical parameters of alloy powder used for preparing Mo$_2$FeB$_2$ cermet by vacuum sintering (VM-Mo$_2$FeB$_2$) are shown in Table 1.

### Table 1. The technical parameters of the alloy powders.

| Powder | Mean Particle Size (μm) | Chemical Composition (wt%) |
|--------|-------------------------|-----------------------------|
| Fe     | 80                      | C < 0.1, N < 0.1, O < 0.2, Bal Fe |
| Ni     | 75                      | Ni ≥ 99.5, C < 0.15, Si < 0.01, Bal Ni |
| FeB    | 120                     | B = 22%, C < 0.27, Si < 0.71, Bal Fe |
| Mo     | 110                     | Fe < 0.002, O < 0.1, Si < 0.001, Bal Mo |
| Cr     | 75                      | O < 0.2, Fe < 0.18, N < 0.045, Bal Cr |

2.1. WM-Mo$_2$FeB$_2$ Preparation

The diameter of the flux-cored wire designed in this study is 3.2 mm, the powder composition of the flux-cored wire is 60 wt.% Mo and 40 wt.% FeB, and the powder filling rate is 70%. The steel strip of flux-cored wire is 304 stainless steel. The technical parameters of the alloy powder are shown in Table 1, and composition of the 304 stainless steel is shown in Table 2.

### Table 2. Chemical composition of 304 stainless steel (wt.%).

| C   | Mn | P  | S  | Si | Cr | Ni |
|-----|----|----|----|----|----|----|
| 0.05| 1.2| 0.015| 0.01| 0.2| 18.5| 9.2|

The preparation process of flux cored wire is as follows:

1. Weigh the alloy powder according to the mass ratio of 60 wt.% Mo and 40 wt.% FeB and then mixed for 10 min to obtain the powder;
2. After 304 stainless steel is cleaned by ultrasonic cleaning equipment, the steel strip is rolled into U-shape by flux cored wire production equipment, and the powder made in step (1) is added into the U-shaped steel strip;
3. The U-shaped groove is closed to make the powder wrapped in it, and the closure part is connected by lap joint; Through wire drawing, drawing and reducing are carried out step by step, and finally the diameter reaches 3.2 mm;
4. The flux cored wire layer obtained in step (3) is wound into a coil to obtain the finished surfacing flux cored wire.
After the flux cored wire is prepared, it is cladding on the Q235 substrate with the arc of the ZX7-315STG argon arc welding machine to prepare WM-Mo₂FeB₂. In the welding process (TIG), pure argon is mainly used as shielding gas, and tungsten electrode moves at the speed of 100 mm/min. After the sample is cooled to room temperature, the second layer and the third layer are deposited on the first layer with the same process parameters to ensure that the cladding layer has a certain thickness, thus reducing the influence of base metal on the dilution of cladding metal. See Table 3 for welding parameters.

### Table 3. Technological parameter of TIG (Argon tungsten arc welding).

| Parameter                  | Value                      |
|----------------------------|----------------------------|
| Protective gas             | 99.9% pure argon           |
| Tungsten diameter; Current | 3.2 mm; 140 A              |
| Voltage                    | 18–20 V                    |
| Flow rate of argon         | 12 L/min                   |
| Speed of welding           | 100 mm/min                 |

2.2. VM-Mo₂FeB₂ Preparation

Commercial Mo powders, FeB powders, Ni powders, Cr powders and carbonyl Fe powders were used as raw materials. Table 4 shows the chemical composition and particle size of the alloy powders.

### Table 4. EPMA (Electron Microprobe) results of 1 zone in VM-Mo₂FeB₂.

| Element | Mass Fraction (%) | Atom Fraction (%) |
|---------|-------------------|-------------------|
| B       | 11.008            | 44.6094           |
| Cr      | 18.376            | 15.4812           |
| Fe      | 21.890            | 17.1708           |
| Ni      | 1.689             | 1.2599            |
| Mo      | 47.038            | 21.4785           |
| Total   | 100               | 100               |

The composition design (mass fraction) of the alloy powders was 42% Mo+28% FeB+5% Cr+3% Ni + balance Fe. Alloy powders were mixed in QM-3SP2 (Shanghai Shupei Experimental Equipment Co., Ltd., Shanghai, China) planetary ball mill for 24 h at a speed of 600 r/min. Polyvinyl Butyral (PVB) (Jinzhou Hongda New material Co., Ltd., Jinzhou, China), which accounted for 3% of the total mass of the alloy powders, was used as binder. The mixture was pressed into pressure machine with dimensions of 400 mm × 40 mm × 4 mm at a pressure of 150 MPa. After drying, it is sintered in a vacuum sintering furnace and the degree of sintering vacuum was 1.0×10⁻² ~ 1.0×10⁻³ Pa. The sintering system is: Increasing the temperature from room temperature to 400 °C at a speed of 10 °C/min, after 30 min incubation, increasing the temperature up to 1050 °C at a speed of 10 °C/min for 30 min, the temperature up to 1210 °C at a speed of 5 °C/min for 30 min, and then cooled to room temperature with the furnace to obtain VM-Mo₂FeB₂.

2.3. Microstructural Investigations and XRD Analysis

To observe its microstructure, the WM-Mo₂FeB₂ and VM-Mo₂FeB₂ were ground with 1500 mesh continuous grade sandpaper and polished by 1.5 μm diamond paste. Then, the specimens were etched using a 20 vol% hydrofluoric acid, 30 vol% hydrochloric acid and 50 vol% nitric acid solution for 10 s. The microstructure was studied with scanning electron microscope (SEM, JSM-6600V, Japanese electronics company, Tokyo, Japan.) in backscattered electron (BSE) mode while analysis of the chemical composition of both hard phase and binder phase was performed by an electron probe micro analyzer (EPMA, JXA-8530F PLUS, Japanese electronics company, Tokyo, Japan). The volume fraction of microstructure constituents was calculated by the Axioimaging software related to Axio
Lab A1 optical microscope. X-ray diffraction (XRD, Jinan, China) was used to analyze the phases of the WM-Mo₂FeB₂ and VM-Mo₂FeB₂.

2.4. Hardness Measurement

The microhardness of hard phases in the WM-Mo₂FeB₂ and VM-Mo₂FeB₂ were texted by a Vickers hardness tester with a load of 0.5 kg for 10 s dwell time. The rockwell hardness of the WM-Mo₂FeB₂ and VM-Mo₂FeB₂ were also measured. At least three points in samples were measured randomly and the average value was set as the final result.

2.5. Wear Tests

For the wear resistance examination, the samples were machined to 31 mm × 7 mm × 5 mm and smoothed the sample surface with abrasive papers to remove metallic oxide of surface. Block on ring wear resistance tests were performed using an MM200 testing machine (Hebei Xuanhua Zhengli Balancing Machine Co., Ltd., Hebei, China) under dry and rotating condition at room temperature. Carburized 20CrMnTi steel with the size of 40 mm in diameter and 10 mm in thickness was selected as the counterpart, whose Rockwell hardness was 60 HRC (Rockwell hardness). The wear test speed was 200 r/min, the load was 150 N and the wear time was 60 min, respectively. The worn morphologies of the samples were analyzed using SEM to determine the wear mechanism.

2.6. Corrosion Resistance Test

Corrosion resistance of the samples was investigated through potentiodynamic polarization on CS350 electrochemical workstation. In this study, a conventional three-electrode system with platinum plate, saturated calomel electrode (SCE) and samples acted as counter electrode, reference electrode and working electrode, respectively. Potentiodynamic polarization tests were implemented in 3.5 wt% NaCl solution at room temperature with a scanning rate of 0.5 mV/s. The scanning range was −0.65 to 0.25 V relative to the open circuit potential (OCP) and at least three sets of measurements of samples were carried out to ensure the repeatability. Moreover, the corrosion morphologies of the WM-Mo₂FeB₂ and VM-Mo₂FeB₂ after the electrochemical tests were investigated by SEM and the composition of the corrosion products produced on the samples was investigated through X-ray photoelectron spectroscopy (XPS, Jinan, China). Photoelectron emission was excited by monochromatic Al Kα (1486.6 eV) source. The C 1s peak from adventitious carbon at 284.8 eV was used as a reference to correct the charging shifts.

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of the WM-Mo₂FeB₂ and VM-Mo₂FeB₂ are shown in Figure 1.
The VM-Mo2FeB2 is mainly composed of γ-CrFeNi and Mo2FeB2 (Figure 1a). No other new phases were formed during the sintering process of ternary borides. At the same time, comparing the diffraction peak intensity of the two main phases, it is found that the diffraction peak intensity of γ-CrFeNi phase is weaker than that of Mo2FeB2 phase, indicating that the content of Mo2FeB2 phase in VM-Mo2FeB2 is relatively higher than that of the γ-CrFeNi phase. In addition, no brittle diffraction was detected in Fe2B. Because of its poor crystallinity [20], the large area segregation of Fe2B brittle phase will destroy the original integrity and continuity of Mo2FeB2-based cermet. Therefore, when subjected to load, cracks will occur and rapidly expand, thus affecting the mechanical properties of the material [21]. Figure 1b shows the XRD diffraction pattern of WM-Mo2FeB2. The results show that the WM-Mo2FeB2 is composed of Mo2FeB2(M3B2), NiCrFe, MoCrFe and Cr2B3. Mo2FeB2 forms M3B2 compound boride with Mo and Cr at high temperature. At the same time, MoCrFe is a solid solution of Mo and Cr dissolved in Fe, while NiCrFe is a solid solution formed by solid solution of Ni and Cr in Fe. Besides the main phase, Cr2B3 boride was also found in the WM-Mo2FeB2. The XRD patterns of the WM-Mo2FeB2 and VM-Mo2FeB2 were compared, and there were some differences between them. On the one hand, the number of phases in the WM-Mo2FeB2 increased rapidly with the appearance of MoCrFe phase and Cr2B3 phase. On the other hand, from the diffraction peak intensity, the content of the Mo2FeB2 hard phase formed in the WM-Mo2FeB2 is obviously lower than that of VM-Mo2FeB2.

In order to further confirm the Mo2FeB2 phase and its main form and distribution in the VM-Mo2FeB2, an electron probe micro analyzer (EPMA) was used to analyze the composition of VM-Mo2FeB2. From the BSE image of VM-Mo2FeB2 (Figure 2), it consisted mainly of a white phase and we performed component analysis on the white phase (one zone in Figure 2); the results are listed in Table 4.
It was found that the white phase was mainly composed of Mo, Fe, B, and Cr and the atomic ratio of Mo, Fe and B did not satisfy 2:1:2. This was because chromium substitutes for Mo and Fe sites in the lattice that form complex borides M₃B₂(M: Mo Fe Cr) according to the reactions [22,23] and the Equations (1) and (2) are as follows:

\[
\text{Cr + Mo}_2\text{FeB}_2 \rightarrow (\text{Mo, Fe, Cr})_3\text{B}_2 \quad (1)
\]

\[
\text{Fe + Fe}_2\text{B} + (\text{Mo, Fe, Cr})_3\text{B}_2 \rightarrow \text{Liquid} + (\text{Mo, Fe, Cr})_3\text{B}_2 \quad (2)
\]

According to the ternary phase diagram of Mo–Fe–B [22], the liquid phase is Fe-B eutectic liquid phase.

Mo₃FeB₃ belongs to the tetragonal lattice [24] and its crystal structure is shown in Figure 3.

The lattice constants of Mo₃FeB₃ are a = b = 5.807 Å, C = 3.142 Å. In Mo₃FeB₃ protocell, there are eight Fe atoms at the vertex position, two at the face center position, four Mo atoms and all located in the cell, and eight B atoms are all on the surface [25].

After analysis, the atomic ratio of M (M: Mo, Fe, Cr) to B is close to 3:2, combined with the XRD pattern, thereby we presume that the white phase is complex ternary boride M₃B₂.

3.2. Microstructure Characterization

The BSE image of VM-Mo₃FeB₃ is shown in Figure 4a.
It can be seen from the figure that most of the VM-Mo$_2$FeB$_2$ is equiaxed, and the volume percentage is significantly higher than that of the bonded phase $\gamma$-CrFeNi. The hard phase particles are smaller and the growth is incomplete, which is due to the lower solid-state sintering temperature in the process of solid-phase sintering. Yu et al. [26] revealed that Mo$_2$FeB$_2$-based cermets will evolve from equiaxed grains of solid phase sintering to flake or columnar shape of liquid phase sintering during sintering. At the same time, it can be seen from the image that there are a lot of pores in the VM-Mo$_2$FeB$_2$, and the density is relatively low. This is because the sintering time is very short, and the liquid phase generated by the eutectic reaction does not have enough diffusion to fill these pores during the solid-liquid transition. Figure 4b–d show the typical microstructure of different areas of WM-Mo$_2$FeB$_2$. It can be seen from the figure that the WM-Mo$_2$FeB$_2$ is mainly composed of various massive, fishbone-shaped and irregular hard phases and eutectic matrix. The hard phase on the surface of the WM-Mo$_2$FeB$_2$ is distributed in the eutectic matrix as coarse blocks (Figure 4b). The coarsening of massive structure can be used to explain this phenomenon, that is the dissolution cycle of hard phase of fine particles in VM-Mo$_2$FeB$_2$ under the action of arc heat, and then through liquid phase diffusion; small hard particles precipitate on the surface of large particles, resulting in the increase of hard phase particle size, which is consistent with the dissolution precipitation mechanism [27]. In the middle layer of the WM-Mo$_2$FeB$_2$, in addition to the thick block hard phase, there are also fishbone-like hard phase connected by slender hard phase. This is mainly due to the inhomogeneous composition of the liquid phase of the alloying elements Mo, Fe, Cr, B in the front of hard phase interface. At the same time, the (100) direction of Mo$_2$FeB$_2$ crystal, that is, the c-axis direction, is the preferred direction for grain growth [28]. The above two factors cause the Mo$_2$FeB$_2$ phase to present a slender shape and connect to form fishbone shape, as shown in Figure 4c. In addition, there is an obvious transition layer near the fusion line in Figure 4d, which indicates good diffusion and metallurgical bonding between the WM-Mo$_2$FeB$_2$ and the substrate. Compared with VM-Mo$_2$FeB$_2$, the amount of the hard phase in WM-Mo$_2$FeB$_2$ is less, and the hard phase is coarser, but there is no obvious porosity, and the microstructure is more dense.

To better analyze the alloying element distribution of the WM-Mo$_2$FeB$_2$, the map scanning images of the WM-Mo$_2$FeB$_2$ with different areas are shown in Figure 5.
Figure 5. Elements distribution of the WM-Mo$_2$FeB$_2$ with different zones: (a) Top layer, (b) Middle layer and (c) Bottom layer.

As we can see from the figure, elemental Mo and B are mainly distributed in the hard phase while elemental Fe is mainly distributed in the matrix. The distribution of Cr and Ni in different regions of the WM-Mo$_2$FeB$_2$ is also different, for the top and middle layers of the WM-Mo$_2$FeB$_2$, elemental Cr and Ni are mainly distributed in the matrix. While at the bottom of the WM-Mo$_2$FeB$_2$, elemental Cr and Ni are uniformly distributed but there is no behavior of segregation.

Figure 6 shows elemental content changes along the longitudinal direction of the WM-Mo$_2$FeB$_2$, the content of Mo decreases sharply from the top layer to the bottom layer of the WM-Mo$_2$FeB$_2$ while the counterpart of Fe element increases dramatically.

Figure 6. Variation of elemental content of along the longitudinal direction of the WM-Mo$_2$FeB$_2$. 
Some reasons can explain this phenomenon: The welding current used in WM-Mo2FeB2 was large (140A) and the heat input was large, which can quickly melt the surface of the carbide-tipped electrode and substrate to form a weld pool. Under the agitation of the arc, the molten liquid substrate and the weld pool of the bottom region mixed so that the concentration of Mo in the bottom layer was greatly reduced while Fe greatly increased. Meanwhile, the flow rate of the liquid metal in the bottom area was relatively slow and temperature was low while the viscosity was large, which made the molten metal of the Mo-rich difficult to flowing to the bottom of the weld pool near the fusion line so that the Mo content was low while the Fe content was higher resulting in a poor Mo rich Fe atmosphere. While the B element slowly increased, possibly due to the lighter mass of B element and small buoyancy while the cooling rate of the welding was faster, some B elements were less than floating and finally remained at the bottom. The deeper the Cr element reached the bottom of the weld pool and the slight decrease in elemental content may be attributed to the dilution of the matrix and the change in Ni element content was relatively not obvious. The concentration of Mo in the top layer was large and Mo2FeB2 easily formed. As the depth increased, Mo2FeB2 gradually decreased, which was basically consistent with the microstructure analysis (Figure 4).

3.3. Phase Evolution in Sintering and Welding

3.3.1. Sintering Phase Evolution

Previous literature studies [29,30] indicated that Mo2FeB2 formed using solid phase in situ reaction between powder particles in the ternary boride solid phase sintering process, and the phase transformations involved in the process are listed as follows, Equations (3)–(5):

\[
\text{FeB} + \text{Fe} = \text{Fe}_2\text{B} \tag{3}
\]

\[
2\text{Mo} + 2\text{FeB} = \text{Mo}_2\text{FeB}_2 + \text{Fe} \tag{4}
\]

\[
2\text{Mo} + 2\text{Fe}_2\text{B} = \text{Mo}_2\text{FeB}_2 + 3\text{Fe} \tag{5}
\]

After milling, the binary boride FeB and the metal powder were thoroughly mixed, as shown in Figure 7a.

![Figure 7. Phase evolution diagram of vacuum liquid phase sintering process (a) Powder mixing, (b) The transformation of FeB, (c) Formation of Mo2FeB2, (d) Growth of Mo2FeB2, (e) Reforming process of Mo2FeB2 particles, (f) Densification of Mo2FeB2.](image-url)
When the temperature arrived 452 °C, the transformation from FeB to Fe₄B occurs (Equation (3)) [30], as shown in Figure 7b. While at 852 °C, the transformation form binary borides to MoₓFeB₂ happens in Mo enrichment atmosphere (Equations (4) and (5)), as shown in Figure 7c and the MoₓFeB₂ hard phases precede the liquid phase formation. At the same time, as the temperature increases further, the diffusion of Mo, B, Fe and other elements accelerates, which makes the MoₓFeB₂ hard phases grow (Figure 7d). Subsequently to the process of liquid phase sintering, the following transformations occur, Equations (6) and (7):

\[
\gamma^-\text{Fe} + \text{FeB} = \text{L}_1 \tag{6}
\]

\[
\gamma^-\text{Fe} + \text{L}_1 + \text{Mo}_2\text{FeB}_2 = \text{L}_2 + \text{Mo}_2\text{FeB} \tag{7}
\]

When the temperature reached 1092 °C, the generation of eutectic liquid phase L₁ (Equation (6)) appeared around MoₓFeB₂ hard phases and dissolved and rearranged MoₓFeB₂ hard phases as well as performed initial densification on the VM-MoₓFeB₂, as shown in Figure 7e. As the temperature increased, Equation (7) applied. MoₓFeB₂ hard phases have a high solubility in the liquid phase L₂ and further densify under the influence of L₂. Finally, the VM-MoₓFeB₂ mainly consists of MoₓFeB₂ hard phase and γ-CrFeNi, as shown in Figure 7f.

3.3.2. Welding Phase Evolution

In the process of argon arc cladding, the formation of MoₓFeB₂ cermet conforms to the nucleation and growth mechanism. The first stage is the full mixing of metal powders. In the second stage, the metal powder gradually melts under the action of welding heat, and then forms the welding pool. According to the Fe–B binary phase diagram [31], the formation temperatures of FeB and Fe₂B are 1650 °C and 1389 °C, respectively. Mo atom in liquid phase reacts with FeB and Fe₂B to form MoₓFeB₂ (equations 4 and 5), and then precipitates hard phase and is covered by liquid phase surface. Under the synergistic effect of high temperature and alloy element concentration, high concentration Cr element in liquid phase diffuses to MoₓFeB₂ (formula 1) [29]. Cr atoms replace Mo and Fe atoms in MoₓFeB₂ lattice, resulting in lattice distortion and effectively improving the crystal structure of MoₓFeB₂ mechanical properties [32]. With the continuous decrease of temperature, element B is basically involved in the formation of boride, rather than the solid solution in the matrix [33]. When the eutectic temperature is reached, the residual liquid phase will solidify to form Fe-Cr matrix.

3.4. Hardness Analysis

Figure 8 shows the Rockwell hardness and Vickers hardness of VM-MoₓFeB₂ and WM-MoₓFeB₂.

![Figure 8. Rockwell hardness and Vickers hardness of VM-MoₓFeB₂ and WM-MoₓFeB₂.](image-url)
In order to make the data accurate, each test data was measured five times, and the average value was considered. At the same time, the standard deviation of the data was analyzed by using the principle of statistics. The final result is shown in Figure 8. The Rockwell hardness of VM-Mo2FeB2 and WM-Mo2FeB2 is 62 HRC and 60.5 HRC respectively. The Vickers hardness is 842.4 HV0.5 and 828.9 HV0.5, respectively. Although the hardness of the WM-Mo2FeB2 decreases, the hardness difference between the VM-Mo2FeB2 and WM-Mo2FeB2 is not obvious, which is mainly due to the increase of the hardness of the matrix by the solution strengthening of chromium, nickel and other alloy elements in the welding process. In addition, the formation of hard phase Mo2FeB2 also improves the hardness of WM-Mo2FeB2. Compared with VM-Mo2FeB2, the hardness of WM-Mo2FeB2 decreases slightly, which is mainly related to the content of hard phase Mo2FeB2. The volume fraction of hard phase was calculated for each sample. Red indicates the matrix phase, and the other color belongs to Mo2FeB2 hard phase (Figure 9).

![Image of Figure 9](image_url)

**Figure 9.** Images of calculation of hard phase fraction: (a) VM-Mo2FeB2, (b) WM-Mo2FeB2.

In Figure 9a, the proportion of Mo2FeB2 hard phase is 76.13%, while in Figure 9b, the corresponding proportion is only 69.05%. The amount of hard phase in VM-Mo2FeB2 is much more than that in WM-Mo2FeB2. Combined with the previous microstructure analysis (Figure 4), it can be found that the number of hard phases in the WM-Mo2FeB2 is significantly reduced, and some hard phases in the VM-Mo2FeB2 are connected with each other, which is the reason why the hardness of VM-Mo2FeB2 is higher than that of WM-Mo2FeB2.

### 3.5. Wear Properties

#### 3.5.1. Wear Measurement

The weight loss and wear time curve of VM-Mo2FeB2 and WM-Mo2FeB2 are shown in Figure 10.

![Image of Figure 10](image_url)

**Figure 10.** Wear weight loss of VM-Mo2FeB2 and WM-Mo2FeB2.
It can be seen that in the first 20 min of the wear test, the weight loss of both is relatively large. This is because it is difficult to achieve the desired smoothness between the contact surface of the specimen and the wearing material. There are randomly distributed micro bumps of different sizes, but the actual contact phenomenon only exists between the micro bumps, and then the stress amplitude modulation phenomenon [34] will appear, resulting in the actual contact area less than the nominal contact area, and each rough body bears more load. According to the mechanical locking theory proposed by Amontons, the dynamic friction is caused by the upper micro convex body passing through the lower micro convex body, which eventually causes the micro convex body to fall off from the material surface and further increase the wear amount. With the wear going on, the asperities gradually wear and the actual contact area increases. After 30 min of wear test, the wear amount enters the stable wear stage, and the wear amount gradually decreases in unit time, and the final wear amount tends to be stable. The wear loss of VM-Mo$_2$FeB$_2$ is 10.5 mg, and the WM-Mo$_2$FeB$_2$ is 2.4 mg. Its wear resistance is better than that of VM-Mo$_2$FeB$_2$. Generally speaking, the wear resistance increases with the increase of hardness and volume fraction of carbide or boride. The hardness and volume fraction of VM-Mo$_2$FeB$_2$ are higher than that of WM-Mo$_2$FeB$_2$. In fact, during the wear process of VM-Mo$_2$FeB$_2$, the bonding force between the hard phase particles protruding from the surface and the matrix is less than the shear stress of the worn surface. Some hard phases fall off from the matrix to form new abrasives, which aggravates the abrasive wear. The results show that the wear resistance is not only related to the hardness and volume fraction of the hard phase, but also to the microstructure and distribution of the hard phase.

3.5.2. Wear Morphologies and Wear Mechanism

Figure 11 shows the wear morphology of VM-Mo$_2$FeB$_2$ and WM-Mo$_2$FeB$_2$.

![Figure 11. Wear morphology of different samples: (a) VM-Mo$_2$FeB$_2$, (b) WM-Mo$_2$FeB$_2$.](image)

In Figure 11a, it can be clearly seen that there are obvious wear grooves around Mo$_2$FeB$_2$, which is the characteristic of abrasive wear. Moreover, wear traces of VM-Mo$_2$FeB$_2$ can be found around Mo$_2$FeB$_2$, which also shows that the wear performance of VM-Mo$_2$FeB$_2$ is inferior to that of WM-Mo$_2$FeB$_2$. In Figure 11b, there is a large amount of wear debris. This is mainly due to the slight deformation of the matrix material under the action of extrusion and shear. Partial deformation causes the atoms in the contact area to approach each other and produce partial adhesion. When the sliding continues, the attachment points are sheared and transferred to the surface of the substrate and fall off to form wear debris, which is a typical feature of adhesive wear.

3.6. Corrosion Resistance Analysis

3.6.1. Polarization Curves

The corrosion behavior of VM-Mo$_2$FeB$_2$ and WM-Mo$_2$FeB$_2$ in 3.5 wt% NaCl solution was studied by potentiodynamic polarization technique. The polarization curve is shown in Figure 12.
Obvious passivation phenomenon is observed in VM-Mo₂FeB₂ and WM-Mo₂FeB₂, and the passivation range is about 0.2 V, indicating the formation of stable passivation film. When the potential increases to about 0 V, the current density increases sharply, which indicates that the passive film breaks and the corrosion behavior continues. Table 5 shows the corrosion parameters obtained from potentiodynamic polarization test.

Table 5. Corrosion parameters of different samples evaluated by potentiodynamic polarization tests in 3.5 wt% NaCl solution.

| Sample         | $E_{\text{corr}}$ (V) | $I_{\text{corr}}$ (μA/cm²) | $E_{\text{pit}}$ (V) |
|----------------|-----------------------|-----------------------------|----------------------|
| VM-Mo₂FeB₂     | −0.38                 | 1.14                        | 0.02                 |
| WM-Mo₂FeB₂     | −0.46                 | 37.6                        | −0.04                |

$E_{\text{corr}}$, $I_{\text{corr}}$ and $E_{\text{pit}}$ represent corrosion potential, corrosion current density and pitting potential, respectively.

From the corrosion potential measurements, the corrosion potential of VM-Mo₂FeB₂ is slightly higher than that of WM-Mo₂FeB₂, which indicates that the corrosion tendency of WM-Mo₂FeB₂ is higher than that of VM-Mo₂FeB₂. From the view of corrosion current density, the corrosion current density of VM-Mo₂FeB₂ is much lower than that of WM-Mo₂FeB₂, which indicates that WM-Mo₂FeB₂ has fast corrosion rate and poor corrosion resistance. Pitting potential is the critical potential which causes the corrosion of metal electrode and the sharp increase of corrosion current density. The pitting potential generally reflects the stability of the passive film. Generally speaking, the higher the pitting potential, the better the stability of the passive film. It can be seen from the results in Table 5 that the pitting potential of VM-Mo₂FeB₂ is higher than that of WM-Mo₂FeB₂, indicating that the passive film of VM-Mo₂FeB₂ is more stable and has better corrosion resistance.

3.6.2. XPS Analysis

The chemical composition of the passive film was studied by XPS. Figure 13 shows the detailed spectra of Fe₂p, O₁s and Cr₂p in the passive film formed on VM-Mo₂FeB₂ and WM-Mo₂FeB₂ in 3.5 wt% NaCl solution.
Figure 13. XPS spectra of Fe 2p, O 1s and Cr 2p for passive films formed on VM-Mo:FeB<sub>2</sub> and WM-Mo:FeB<sub>2</sub> in 3.5 wt% NaCl solution: (a) Fe 2p, (b) O 1s and (c) Cr 2p.

As we can see, the passive films of VM-Mo:FeB<sub>2</sub> and the WM-Mo:FeB<sub>2</sub> both have the same chemical composition and the observed XPS pattern indicates the presence of iron, chromium, oxygen in the passive film. The spectra of Fe2p (Figure 13a) shows the presence of two components: metallic, Fe<sup>0</sup> (706.6 eV) and Fe<sup>2+</sup>O<sub>3</sub> (710.9 eV) [35,36]. The spectra of O1s (Figure 13b) indicates two components: oxide and hydroxide. The peak at 531.3 eV corresponds to OH<sup>-</sup> in the hydroxide and a second one 530.2 eV corresponds to O<sup>-</sup> in the oxide [35]. In Cr2p spectra (Figure 13c), two components can be observed: Cr<sup>3+</sup> in Cr:O<sub>3</sub> (576.5 eV) and Cr<sup>3+</sup> in Cr(OH)<sub>3</sub> (577.2 eV) [35]. Therefore, the components of the passive film are mainly Fe:O<sub>3</sub>, Cr:O<sub>3</sub> and Cr(OH)<sub>3</sub>.

3.6.3. Corrosion Morphologies

Corrosion morphologies of VM-Mo:FeB<sub>2</sub> and WM-Mo:FeB<sub>2</sub> after potentiodynamic polarization test are shown in Figure 14. As can be seen from the figure, the corrosion is likely to occur at the boundaries between the Mo:FeB<sub>2</sub> phase and the iron matrix and tends to the matrix with less Mo content. This is because the Mo:FeB<sub>2</sub> hard phases itself have good corrosion resistance [37], which reduce the corrosion of chloride ions in the solution. Moreover, the corrosion resistance of a certain material is usually closely related to the chemical composition. As is well known, chemical elements such as Cr and Mo are the crucial factors to improve the pitting corrosion resistance of stainless steel. They do not only reduce the generation capacity of pitting nuclear but also decrease the growth rate of pitting pits [38]. Compared with hard phases, the less solid solution Cr and Mo elements in the matrix and the uneven distribution of element components caused by liquid weld pool, which lead to corrosion occurs on the matrix where the content of Cr and Mo is
small. In addition, compared with VM-Mo:FeB₂, the size of the corrosion pits of the WM-
Mo:FeB₂ is relatively larger. This is because the liquid weld pool has a short duration and
insufficient element diffusion during the welding process, which make the element distribu-
tion uneven resulting in poor corrosion resistance of the WM-Mo:FeB₂ in the areas with
poor Cr and Mo elements. XPS analysis (Figure 13) shows that the passive film (Cr₂O₃,
etc.) on the surface of the WM-Mo:FeB₂ in those area is not sufficient to block the penetra-
tion of reactive anions (Cl⁻), which penetrate through the passive film to further corrosion
and appear pitting spots. Under the continuous action of anode current, reactive anions
(Cl⁻) migrate and accumulate at pitting spots and the metal matrix will be deeply etched
downward resulting in pitting pits. As the corrosion reaction continues, the dissolved
metal ions will increase continuously and under the influence of the downward gravity
of the corrosion medium, the pitting pits will expand and develop towards the depth di-
rection.

![Figure 14. Corrosion morphologies of VM-Mo:FeB₂ and WM-Mo:FeB₂: (a) VM-Mo:FeB₂ and (b)
WM-Mo:FeB₂.](image)

4. Conclusions

In this study, 304 stainless steel strips and appropriate amounts of powder were used
to make flux cored wire. WM-Mo:FeB₂ was obtained by argon arc welding on Q235 sub-
strate. VM-Mo:FeB₂ was synthesized in situ by vacuum liquid phase sintering. The micro-
structure and properties of WM-Mo:FeB₂ and VM-Mo:FeB₂ were systematically studied.
The results are summarized as follows:

1. The VM-Mo:FeB₂ is mainly composed of γ-CrFeNi and Mo₇FeB₇, and the WM-
Mo:FeB₂ is mainly composed of Mo₇FeB₇ (M:Mo), NiCrFe, MoCrFe and Cr:B₇. The hard
phase of Mo₇FeB₇ in VM-Mo:FeB₂ is equiaxed, while the WM-Mo:FeB₂ is mainly com-
posed of massive, fishbone and irregular Mo₇FeB₇ hard phases. The amount of hard
phase in VM-Mo:FeB₂ is more than that in WM-Mo:FeB₂.

2. Some pores will be produced in the sintering process of VM-Mo:FeB₂, which affects
the final properties. There is a good diffusion and metallurgical bonding between the
WM-Mo:FeB₂ and the matrix, and the microstructure is more compact.

3. The hardness of VM-Mo:FeB₂ is higher than that of WM-Mo:FeB₂ due to the higher
content of hard phase in VM-Mo:FeB₂, but there is little difference between them.
However, the wear resistance is not only affected by the hardness and volume frac-
tion of the hard phase, but also by the morphology and distribution of the hard phase.
In the wear test of VM-Mo:FeB₂, some hard phases fall off from the surface of the
substrate to form abrasives, which aggravate the wear and make its wear resistance
lower than that of WM-Mo:FeB₂.

4. The results show that the corrosion resistance of VM-Mo:FeB₂ is better than that of
WM-Mo:FeB₂. The passive films formed on VM-Mo:FeB₂ and WM-Mo:FeB₂ are
Fe₂O₃, Cr₂O₃ and Cr (OH)₃.
The microstructure and properties of VM-Mo2FeB2 produced by sintering and the WM-Mo2FeB2 formed by argon arc welding are systematically studied. It is found that it is feasible to perform cladding on a Q235 substrate by preparing flux cored wire and argon arc welding. In terms of practicability, vacuum sintering can only be used for ordinary cylinders and cuboids, so it is difficult to prepare large curved surface and large size cermets workpieces. Argon arc welding is a good solution to this problem; it is easy to operate and flexible in application. Therefore, through the preparation of flux cored wire, the preparation of cladding layer by welding should be popularized.

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