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Effects of extra boron addition on the liquid-state sintering process and properties of hard Mo_2FeB_2-based cermets

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ABSTRACT

The effects of extra boron addition on the sintering mechanism, microstructure, and mechanical properties of Mo_2FeB_2-based cermets, prepared by in-situ liquid reaction sintering method, have been investigated. The results indicate that suitable boron addition effectively lowered the initial liquid-phase sintering temperature of the cermets, and a suitable boron addition contributed to the formation of homogenous and dense structure. As the result, the hardness, transverse rupture strength, and abrasion resistance of the Mo_2FeB_2 cermets were significantly improved. The suitable amount of boron addition into the raw material was around the range of 1–2 wt.%.

1. Introduction

Ternary boride based cermets and their industrial applications have attracted much attention [1–2] due to their wide range of properties such as excellent corrosion resistance, heat resistance, fracture toughness, high strength and hardness. These cermets have been successfully applied to wear-resistant conditions such as injection molding machine parts, can tools making and dies of hot copper extruding [3]. Among these cermets, the Mo_2FeB_2 based cermets consists of Mo_2FeB_2-type ternary boride as a hard phase and a Fe binder phase, and shows superior intrinsic mechanical properties and economic benefits over the other two kinds of cermets, which attracts more attention than the others. But, as a traditional way to prepare this cermets, the thermal spraying technology would inevitably harm the substrate due to the flame temperature of most thermal spraying technologies is higher than 2000 °C [4–6]. Therefore, it is essential to lower the reacting temperature of the cermets [7]. Reaction boronizing sintering associated with in-situ reaction method is a novel strategy to form ternary boride cermets in metal matrix during liquid phase sintering in which the generation of liquid phase makes it possible to reduce the reacting temperature of the cermets. Due to the high reactivity with other metals [8], binary borides have been successfully used as raw materials for preparation of Mo_2FeB_2, Mo_2NiB_2 and WCoB based cermets [1].

Two primary stages are involved in the sintering process, solid- and liquid-state sintering. In the first stage, the elementary chemical reactions of Mo_2FeB_2-based cermets are described as follows:

$$Fe + FeB \rightarrow Fe_2B;\ 452^{\circ}C \quad (1)$$

$$2Mo + 2FeB \rightarrow Mo_2FeB_2 + Fe;\ 852^{\circ}C \quad (2)$$

$$2Mo + 2Fe_2B \rightarrow Mo_2FeB_2 + 3Fe;\ 927^{\circ}C \quad (3)$$

According to Ide and Ando's study [8], the hard phase Mo_2FeB_2 was produced initially by reaction (2) and later by the reaction (3). This stage is the key of the sintering sequence. At the liquid-state sintering stage, by raising the temperature the liquid phases (L_1 and L_2) occurred according to the following reactions:

$$\text{Austenite} + Fe_2B \rightarrow L_1;\ 1092^{\circ}C \quad (4)$$

$$\text{Austenite} + L_1 + Mo_2FeB_2 \rightarrow L_2 + Mo_2FeB_2;\ 1142^{\circ}C \quad (5)$$

At this stage, primary densification by L_1 and secondary densification by L_2 occurs respectively. Once the initial liquid phase L_1 is formed,

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Table 1
Compositions of the Mo_2FeB_2-based cermets samples (wt.%).

Cermets no.	B	Mo	FeB	Fe
1	–	48	40	Bal.
2	0.66	48	40	Bal.
3	1.32	48	40	Bal.
4	1.98	48	40	Bal.
5	2.64	48	40	Bal.

the further formation and spreading over the grains is fast due to surface energy reasons [9]. As soon as L_1 penetrates the particle boundaries, considerable densification is developed by capillary force which leads to particle rearrangement. When the rearrangement process has been completed, L_2 is formed to induce solution-precipitation due to different solubility between the contact points of particles and other solid surfaces. Although, solution-precipitation of particles occurs concurrently with rearrangement which then leads to the formation of the solid skeleton [7], the particle rearrangement dominate the primary densification [10]. Therefore, the L_1 phase plays an important part in reaching full density. In order to lower the sintering reaction temperature, it is necessary to induce the formation of L_1 at a lower temperature. Most of the previous studies are focused on the effects of added reinventing elements [1,11–15] and other compositions [16,17] on the microstructure and mechanical properties. Although B is an important component of Mo_2FeB_2 hard phase, little attention has been devoted to the effects of extra boron addition on the initial liquid phase temperature, and the relationship between the initial liquid phase temperature and the microstructure and mechanical properties of the cermets.

In the present work, Mo_2FeB_2-based cermets samples with different concentrations of added boron were prepared. The effects of different amounts of extra boron additive on the generating temperature of the liquid phase, microstructure and mechanical properties of Mo_2FeB_2-based cermets were investigated.

2. Experimental procedure

The compositions of Mo_2FeB_2-based cermets samples with different boron addition are listed in Table 1. Commercially available FeB, Mo, B, and carbonyl Fe powders were used as raw materials. Characteristics of these raw materials are listed in Table 2. The compositions of the samples were Fe–48Mo–40FeB-xB (wt.%). The boron content (x) varied from 0 to 2.64 wt.% with increments of 0.66 wt.%.

In protective high-purity argon gas atmosphere, the raw powders were mixed in a high-energy planetary ball-mill for 5 h at a rotation speed of 300 rpm with Φ5 mm and Φ10 mm standard stainless steel grinding balls. After milling, the powders were sieved through 200 meshes and then pressed into green compacts with the size of Φ22 mm × 20 mm at 300 MPa for 60 s. The green compacts were then sintered under an argon atmosphere at 1 atm. Based on the chemical reaction process and the reaction rate of Mo_2FeB_2 based cermets (Eq. (1)–(5)), a master sintering curve was designed, as shown in Fig. 1. The holding time for each stage of the solid-state reaction in the sintering process was extended to 90 min to ensure the completeness of the reactions.

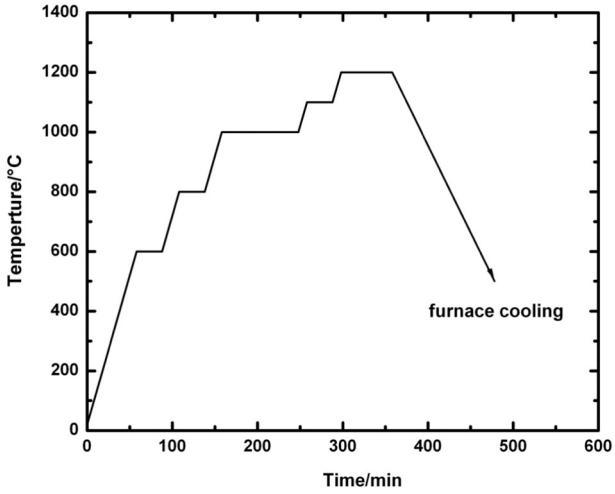

Fig. 1. Master sintering curve of Mo_2FeB_2 based cermets.

The phase composition and the microstructure of all the samples were examined by X-ray diffraction with Cu Kα radiation (XRD, D8 FOCUS) and by scanning electron microscopy (SEM, Hitachi S4800), respectively. The liquid reaction temperatures of the cermets with size of Φ5 mm × 2 mm were measured in the alumina crucible by a Differential scanning calorimetry (Netzsch DSC 404C) at heating rate 0.167 Ks^{-1} in free flow of argon. The testing temperature ranged from 25 °C to 1200 °C. The distribution of the elements was analyzed by energy dispersive X-ray analysis (EDX, GENESIS XM2) combined with the SEM. Porosity were determined by a metallographic microscope (GX51) observation method according to ISO 4505 standard. The average aspect ratio of the hard phase particles were obtained by the image analysis software by Image-pro-plus. The diameter X of the equivalent circle was calculated to represent the mean grain size. To ensure the statistically results, >500 grains per sample were measured. The density of the cermets was measured using Archimedes' method. The relative density of the cermets was calculated by the proportion of the measured density to the theoretical density. Additionally, the abrasion resistance was measured for 120 min on wear and abrasion test machine (M-2000) with a GCr12 abrasive wheel with a diameter of 43 mm. The rotation speed of the wheel was 400 r/min and the load was 10 kg. The traverse rupture strength(TRS) and hardness were measured at room temperature. The TRS was measured from a three-point bending test on a standard experiment machine (CSS-44100) with sample's size of 5 mm × 5 mm × 25 mm. The hardness was evaluated with a Vickers hardness tester (MH-6).

3. Results and discussion

3.1. Phase composition

The results of X-ray diffraction (XRD) are shown in Fig. 2. All the Mo_2FeB_2-based cermets contain two main phases: the Mo_2FeB_2 hard phase and the ferrous binder phase. Traces of Fe_2B phase began to appear in the cermets as the content of boron additive increased to 1.32 wt.%.

Table 2
Characteristics of the raw materials.

Powder	Mean particle size (μm)	Chemical composition (wt.%)	Manufacturer
Mo	3	Mo ≥ 99.9	Beijing Xing Rong Yuan Technology Co., Ltd. of China
Fe	44	Fe ≥ 99.5	Beijing Xing Rong Yuan Technology Co., Ltd. of China
B	74	B > 99.0	Tianjin jinke chemical research institute of China
FeB	74	S ≤ 0.012, P ≤ 0.027, C ≤ 0.41, Si ≤ 0.23	Sichuan Kehui Industrial Corp. Ltd. of China