The effect of alloying on the microstructure and mechanical properties of Mo-Fe-B boride hard alloys

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Abstract. Mo2FeB2 based cerments with different Cr and Ni contents were prepared by liquid phase sintering. The effects of Ni and Cr content on the microstructure, hardness and fracture toughness were investigated. The results reveal that alloying of cermet with nickel leads to formation of structure characterized by high austenite volume fraction and low ferrite content. As a consequence Cr predominantly dissolved in Mo2FeB2 boride lattice. Synthesized cerments have a superior combination of hardness and fracture toughness.

1. Introduction

Hard alloys based on ternary borides (Mo2FeB2 and Mo2NiB2) are potential candidates for partial substitution of hard alloys based on tungsten carbide in the industry. These hard alloys (cerments) have excellent combination of hardness, toughness, corrosion resistance, and a coefficient of thermal expansion close to steel [1, 2]. Mo2FeB2 based cerments attract much attention because of cheap raw material and simple preparation method. This method is known as boronizing sintering and associated with formation of ternary boride cerments in metal matrix during liquid phase sintering [3]. Generation of liquid phase makes it possible to reduce the reacting temperature and consequently reduce temperature of the cerments production.

2. Materials and Methods

2.1. Materials

The compositions of the test materials are listed in table 1. Cerments were supplied by “SpetsInstrument” Co. LLC (Belgorod, Russia). All the samples were produced by powder metallurgical route by blending of the raw materials in benzine, drying, pressing and sintering in a vacuum 10^-2 Pa at 1443 K for 10 minutes.

| Table 1. Compositions of the Mo2FeB2 -based cerments samples (wt.%). |
|-------------------|---|---|---|---|---|
| Alloy             | Mo | B | Cr | Ni | Fe |
| 2Cr2Ni            | 55 | 7 | 2  | 2  | Bal.|
| 2Cr4Ni            | 55 | 7 | 2  | 4  | Bal.|
| 3Cr3Ni            | 55 | 7 | 3  | 3  | Bal.|

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2.2. Analysis

The microstructure and phase composition of the cermetts were studied by means of X-ray diffraction (XRD, ARL XTRA), scanning electron microscopy (SEM, Quanta 600FEG, FEI) and energy dispersive spectrometer (EDS, integrated into SEM Pegasus 2000 system). The mean size of crystals and volume fraction of the hard phase were obtained by the image analysis software Digimizer. To ensure the statistically results, more than 300 grains per sample were measured.

The hardness of the materials was measured using Vickers hardness indenter with a 30 kgf load.

The Palmqvist method was used to determine the fracture toughness of investigated materials. Seven indentations for each hard alloy were carried out on diamond polished surfaces. A 1 mm distance between indentations was kept in order to avoid overlapping effects. Indentation load \( (P) \) was 60 kgf. Lengths \( (L) \) of cracks were measured by light optical microscopy (Olympus GX71). Palmqvist fracture toughness was assessed from equation \( [4] \),

\[
K_{1c} = AH^{0.5} (P/\Sigma L)^{0.5}
\]

where \( H \) is the hardness (N/mm\(^2\)), \( P \) is the applied load (N), \( \Sigma L \) is the sum of crack lengths (mm), \( A \) is a constant with value of 0.0028 \([5]\).

Prior to the microstructure investigation and Palmqvist test, the cermetts were polished with 320 grit SiC abrasive paper and then polished by diamond colloidal suspension (9 \( \mu \)m \( \rightarrow \) 3 \( \mu \)m) on a polishing cloth.

Contiguity was measured in two dimensions by quantitative analysis of SEM images based on the number of intercepts per unite length of test line \( N \).

\[
C_{ss} = 2N_{ss}/(2N_{ss} + N_{sl})
\]

\( N_{ss} \) denotes a number of solid-solid intercepts, \( N_{sl} \) denotes solid-binder (liquid) intercepts \([6]\).

![Figure 1. XRD patterns of Mo\(_2\)FeB\(_2\) based cermets: 1 – 2Cr2Ni; 2 – 2Cr4Ni; 3 – 3Cr3Ni.](image-url)
3. Results

3.1. Phase composition
Figure 1 shows XRD patterns of M₀₂FeB₂ based cermets. It can be seen that all investigated M₀₂FeB₂-based cermets contain M₀₂FeB₂ hard phase and the ferrous binder phase. As far as chromium has ferrite stabilizing effect and nickel is an austenite stabilizer the binder phase is presented by υ-Fe and γ-Fe. The increase of the nickel concentration leads to the increase of the fraction of austenite in a binder. The binder contains ferrite and austenite in 2Cr2Ni and 2Cr4Ni alloys. The alloy 3Cr3Ni is characterized by austenite only binder phase.

Figure 2. Microstructure images of cermets (a, b) 2Cr2Ni; (c, d) 2Cr4Ni; (e, f) 3Cr3Ni.
3.2. Microstructure

Figure 2 shows the microstructure of cermets with various Cr and Ni contents. The bright phase is Mo\textsubscript{2}FeB\textsubscript{2} boride and the dark phase is a solid solution based on iron (ferrite and/or austenite). According to EDS (figure 3) nickel is predominantly located in austenite. Chromium can dissolve both in a binder phase and in a boride too. EDS shows that in alloys 2Cr2Ni chromium is mainly located in ferrite. The increase of the nickel concentration (2Cr4Ni alloy) leads to formation of the structure characterized by the high austenite volume fraction and the low ferrite content. As a consequence Cr predominantly dissolved in the Mo\textsubscript{2}FeB\textsubscript{2} boride lattice in 2Cr4Ni alloy (figure 4).

As it can be seen from SEM images (figure 2) 2Cr2Ni and 2Cr4Ni alloys have a different volume fraction of the binder phase: 22 and 12\% respectively. 2Cr4Ni cermet have large areas free of hard phase crystals. Table 2 shows that these hard alloys have almost the same mean size of boride crystals and a contiguity ratio.

Simultaneous increase of chromium and nickel concentrations leads to formation of microstructure characterized by 15\% volume fraction of binder phase. Binder phase is homogeneously distributed between boride crystals. This alloy is characterized by almost complete absence of areas free of hard phase crystals (figures 1 e–f). 3Cr3Ni cermet has lowest contiguity ratio (table 2) among investigated hard alloys.

| Table 2. Mean size of boride crystals (d) and a contiguity ratio (C\textsubscript{SS}). |
|-----------------|-----------------|-----------------|
| Alloy           | Microstructure parameter |
|                 | d, \mu m         | C\textsubscript{SS} |
| 2Cr2Ni          | 1.5±0.2          | 0.45             |
| 2Cr4Ni          | 1.3±0.2          | 0.45             |
| 3Cr3Ni          | 1.3±0.2          | 0.39             |
3.3. Hardness and fracture toughness

Figure 5 shows a comparison of hardness and fracture toughness of sintered alloys and different WC-Co alloys (colored area). It should be specially pointed out that data for WC-Co alloys were obtained for an indenter load of 30 kgf.

![Fracture toughness vs hardness for a range of hardmetals](image)

Figure 5. Fracture toughness vs hardness for a range of hardmetals [7, 8].

The data for cermets on the base of Mo$_2$FeB$_2$ boride were obtained at applied load of 60 kgf. It is known that the hardness and fracture toughness values reduce with increasing of test force [9]. Therefore, cermets investigated in this work fall into the region with superior mechanical characteristics.

4. Discussion

As it can be seen from the table II and figure 5 neither boride particles size nor contiguity ratio have no considerable correlation with the hardness to toughness ratio of the investigated cermets.

The toughness and the hardness of cermets with various substitutions of iron by nickel and chromium are mainly determined by the phase composition of the binder, e.g. by the presence and the volume fraction of austenite. Thus the minor alloyed with Ni and Cr cermet 2Cr2Ni shows the highest hardness, while more alloyed ones (2Cr4Ni and 3Cr3Ni) are sufficiently tougher.

Within the same binder phase composition (austenite) chromium has much more effect on the hardness, then nickel. While preserving the same total alloying level the cermet with additional Cr content (3Cr3Ni) is harder than the other one with Ni (2Cr4Ni). This fact can be attributed both to the strong strengthening effect of Cr on the hardness of ternary boride Mo$_2$FeB$_2$ [10] and any austenitic steel (which is playing here the role of the metal binder phase).

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