

Development of very high strength Mo_2NiB_2 complex boride base hard alloy

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Abstract

A previous investigation revealed that additions of Cr and V to the Mo_2NiB_2 complex boride base hard alloy changed the boride phase crystal structure from orthorhombic to tetragonal and resulted in a remarkable improvement of mechanical properties associated with microstructural refinement. Moreover, an addition of Mn turned out to be effective in further improvement of the mechanical properties in the V-containing alloy. In this investigation, Ni-5B-xMo-12.5V-2.5Mn (mass%) model alloys with four levels of Mo contents corresponding to Mo/B atomic ratio ranging from 1.0 to 1.3 were prepared to study the effect of the Mo/B atomic ratio on the mechanical properties and microstructure. The results indicated that transverse rupture strength (TRS) increased with increasing Mo/B atomic ratio and showed a maximum value of 3.2 GPa at Mo/B=1.2 and then decreased with increasing atomic ratio. Hardness increased linearly from 86.8 HRA to 90.8 HRA with increasing Mo/B atomic ratio.

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1. Introduction

The wear-resistant applications of hard materials have demanded for not only wear resistance, but also various kinds of characteristics such as corrosion resistance, heat resistance, fracture toughness, high strength and hardness at a wide range of temperatures.

The WC-base cemented carbide is well known as a hard material. In a corrosive environment or at high temperatures, however, this material has shortcomings for usage because of its insufficient corrosion resistance, strength or hardness. For the replacement of the cemented carbides, although borides were expected as promising candidates of the wear-resistant materials, their poor sinterability and extreme brittleness retarded their application as wear-resistant materials.

Recently liquid phase sintering was applied to boride base cermets, namely “reaction boronizing sintering”, at which ternary borides were formed in a metal matrix during in situ sintering reaction; these have been

developed and have introduced some hard alloys with such borides as Mo_2FeB_2 , Mo_2NiB_2 and WCoB. These new hard alloys have been successfully applied to wear-resistant applications such as injection molding machine parts, aluminum die casting machine parts and copper extruding dies, and so on due to their unique properties such as less aggression to mating materials in sliding wear [1].

In these hard alloys, the Mo_2NiB_2 complex boride base hard alloy consists of Mo_2NiB_2 -type ternary boride as a hard phase and a Ni base binder, and shows excellent corrosion resistance. Previous investigations revealed that the addition of Cr and V to the alloy changed the boride structure from orthorhombic to tetragonal and resulted in remarkable improvement of mechanical properties such as transverse rupture strength (TRS), hardness and microstructural refinement [2,3]. It also turned out that the addition of Mn to the alloys resulted in an effective improvement of the mechanical properties and the microstructure. In the V-added hard alloy, the TRS reached a maximum value of 3.5 GPa associated with size refinement and homogeneous distribution of the Mo_2NiB_2 complex boride [4].

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The purpose of this present investigation is to study the effect of Mo content on the mechanical properties and microstructure and to deepen the understanding of the structure–property relationship of the V- and Mn-added high strength Mo_2NiB_2 complex boride base hard alloy.

2. Experimental procedure

Fig. 1 shows the production process of the Mo_2NiB_2 complex boride base hard alloy. Table 1 gives the compositions of Ni–5B– x Mo–12.5V–2.5Mn (mass%) model hard alloys with four levels of Mo content from 1.0 to 1.3 as Mo/B atomic ratio.

The powder mixtures prepared from pure Mo, Mn, carbonyl Ni, VB and Ni_2B were ball-milled in acetone to an average particle size of about 1 μm . After drying, the milled powders were pressed to green compacts and sintered in vacuum for 20 min at a temperature between 1533 and 1613 K. To reduce the oxides on the powder surface, 0.5 mass% of graphite was added as a sintering aid. TRS and hardness (Rockwell “A”) of the sintered compacts were measured. The TRS tests were conducted on $4.0 \times 8.0 \times 25 \text{ mm}^3$ test bars in three-point loading with a 20 mm span. Ten specimens were tested for each composition. The microstructure of the sintered hard alloys was investigated by means of an X-ray diffraction (XRD), scanning electron microscopy (SEM) and image analyzer.

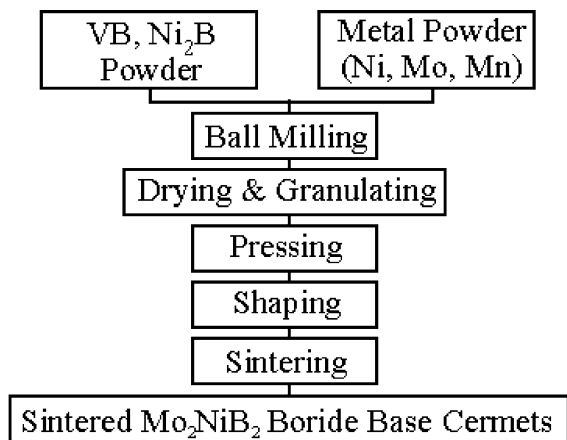


Fig. 1. Schematic flow chart of the production process of Mo_2NiB_2 complex boride hard alloys.

Table 1
Compositions (mass%) of the investigated Mo_2NiB_2 base hard alloys

Mo/B	B	Mo	V	Mn	Ni
1.0	5.0	44.4	12.5	2.5	Bal.
1.1	5.0	48.8	12.5	2.5	Bal.
1.2	5.0	53.2	12.5	2.5	Bal.
1.3	5.0	57.6	12.5	2.5	Bal.

3. Results and discussion

3.1. Mechanical properties

Fig. 2 shows the TRS at each Mo/B atomic ratio as a function of sintering temperature. The hard alloys with Mo/B atomic ratio of 1.1 and 1.2 show higher TRS over a wider range of sintering temperature than the others. The optimum sintering temperature where the maximum TRS was obtained became higher with increasing Mo/B atomic ratio.

Fig. 3 shows the maximum TRS together with the hardness of the model hard alloys sintered at the optimum temperature as a function of the Mo/B atomic ratio. TRS reaches a maximum of 3.25 GPa at Mo/B atomic ratio of 1.2 and then decreases with increasing

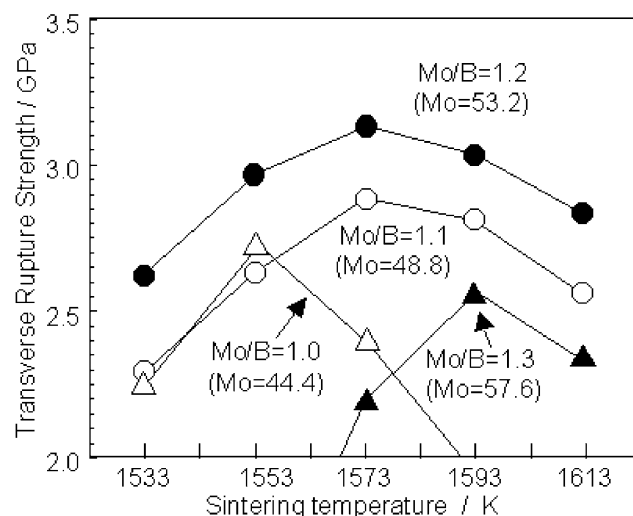


Fig. 2. TRS of the Ni–5B– x Mo–12.5V–2.5Mn hard alloys as a function of sintering temperature.

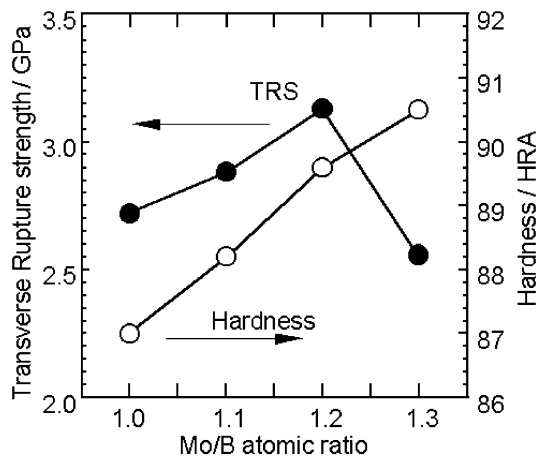


Fig. 3. TRS of the Ni–5B– x Mo–12.5V–2.5Mn alloys sintered at optimum temperatures as a function of Mo/B atomic ratio. Hardness values shown in the figure were measured using the TRS specimens.

Mo/B atomic ratio, while the hardness increases linearly up to 90.8HRA with increasing Mo/B atomic ratio.

3.2. X-ray diffraction

The XRD results shown in Fig. 4 indicate that all the model hard alloys consist of the main constituents of the tetragonal Mo_2NiB_2 complex boride and a Ni base binder. A small amount of the orthorhombic Mo_2NiB_2 is also identified in the alloy with Mo/B atomic ratio of 1.0, while the alloy with Mo/B atomic ratio of 1.3 contains a small amount of Mo and V–Mn intermetallic compound in addition to the main constituents.

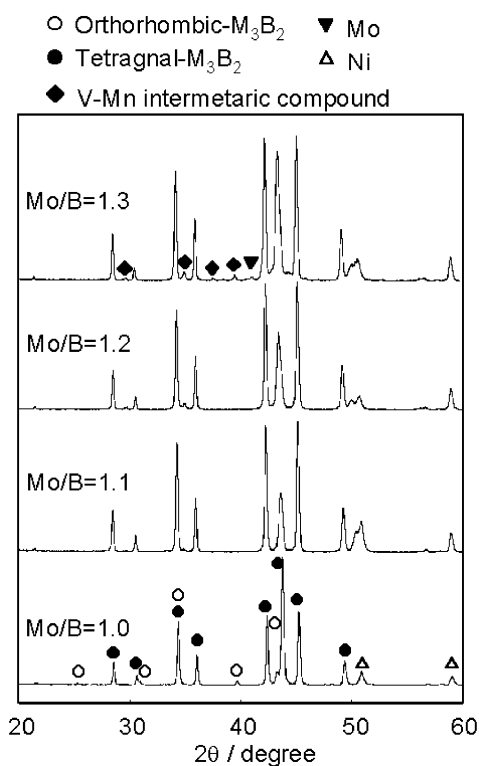


Fig. 4. Cu- K_α XRD patterns of Ni-5B- x Mo-12.5V-2.5Mn alloys with Mo/B atomic ratios from 1.0 to 1.3.

3.3. Microstructure

Fig. 5 shows the back-scattered electron images (BEI) of the model hard alloys. In these BEI, the Ni base binder appears dark and the Mo_2NiB_2 complex boride phase appears gray. The particle size of the Mo_2NiB_2 boride decreases with increasing Mo/B atomic ratio, but at an Mo/B atomic ratio of 1.3, the white third phase is observed to bridge the boundary between the Mo_2NiB_2 complex boride grains. Moreover, several micro-pores are observed at the Mo/B atomic ratio of 1.3.

Considering the XRD result, the white third phase seems to be a Mo alloy. The rectangular boride grain at Mo/B atomic ratio of 1.0 is the orthorhombic Mo_2NiB_2 and round grains are the tetragonal Mo_2NiB_2 . These structures indicate that an increase of the Mo content suppresses the grain growth of the boride probably due to the decrease of interfacial energy between the boride and Ni base binder.

3.4. Structure–property relationship

To study the structure–property relationship, the mean particle size and the contiguity of the boride phase were measured by an image analyzer as shown in Fig. 6. The mean particle size decreases from 2.1 to 0.9 μm with increasing Mo/B atomic ratio. The contiguity of the boride decreases up to the Mo/B atomic ratio of 1.2 and then increases drastically at the ratio of 1.3. High TRS value at the ratio of 1.2 is attributed to the refinement and uniform distribution of the boride grains. The decrease of TRS at the ratio of 1.3 resulted from an increase of the contiguity and the aggregation of boride and white grain phases. Actually, fracture surface observation revealed that the coarse aggregate of boride and the white grains were observed at the fracture origin of the alloy at 1.3. In addition, some pores were also detected at the fracture origin, while no distinct fracture origin was observed in the alloy at the ratio of 1.2. Fig. 7 shows the result of thin foil electron micrographs and EDS spectra analyzed at three points

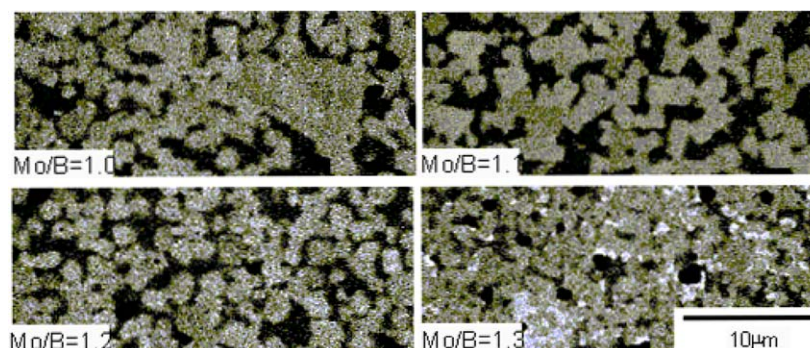


Fig. 5. SEM micrographs of Ni-5B- x Mo-12.5V-2.5Mn alloys with Mo/B atomic ratios from 1.0 to 1.3.

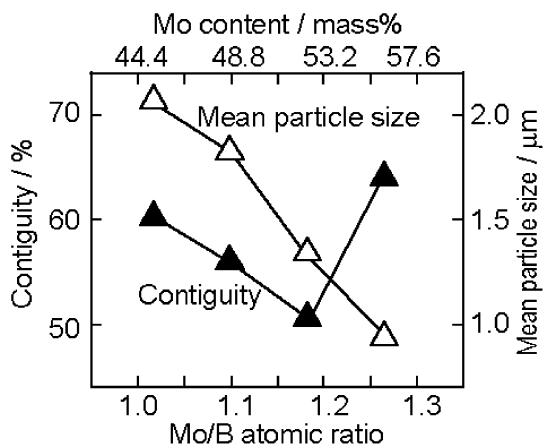


Fig. 6. Effect of Mo/B atomic ratio on the mean particle size and the contiguity of the boride particles.

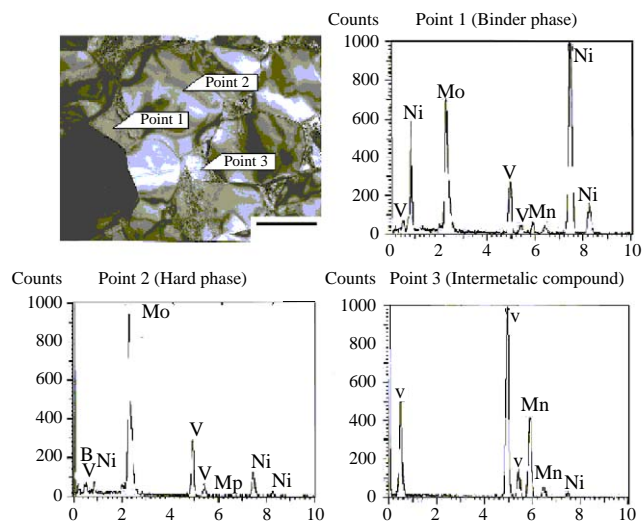


Fig. 7. TEM micrograph of Ni–53.2Mo–12.5V–2.5Mn alloy at Mo/B atomic ratio of 1.2 and EDS analysis results at the indicated points.

of the alloy with high TRS value at the ratio of 1.2. Mo addition contributed not only to the formation of the complex boride (Point 2), but also to the dissolving and strengthening of the Ni base binder (Point 1). Point 3 revealed that a tiny V–Mn intermetallic compound, which was found at the ratio of 1.3 by XRD and SEM observations, was also present in the alloy at the ratio of 1.2. When assuming that V and Mn are partitioned equally in the boride and the binder phases, the approximate composition region of the used model alloys is shown as a gray oval in the isothermal cross-section of the Mo–Ni–B ternary system at 1073 K in Fig. 8. This figure suggests that the Ni base binder phase changes from a Ni base solid solution to a Ni–Mo intermetallic compound or a Mo base solid solution with increasing Mo/B atomic ratio. It seems that the Mo peak observed in the XRD pattern at a ratio of 1.3 represents this phase change of the binder. By the way, the liquid phase sintering of this hard alloy accompanies

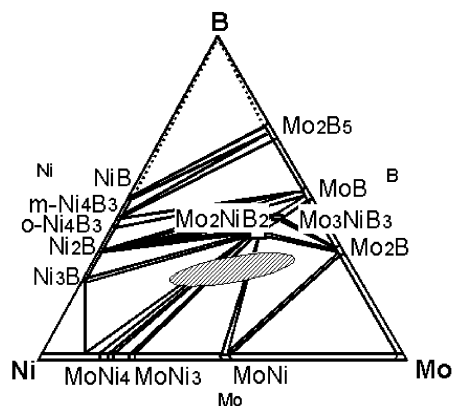


Fig. 8. Isothermal cross-section (mol%) of Mo–Ni–B phase diagram at 1073 K. The region of studied compositions is presented as a gray oval.

the quasi-eutectic reaction between the complex boride and the Ni base metal binder. The pores observed at the ratio of 1.3 may be attributed to poor wettability and an insufficient amount of a liquid phase during sintering due to the composition change of the binder phase.

On the other hand, the increase of hardness by Mo additions is due to the reduction of the mean free path of the binder phase caused by particle refinement as well as a solution strengthening by Mo in the Ni base binder.

Consequently, the microstructure consisting of the tetragonal complex boride and solution strengthened Ni base binder obtained at the Mo/B atomic ratio of 1.2, which resulted in an excellent TRS and hardness in the hard alloys.

4. Conclusions

The composition of Ni–5B– x Mo–12.5V–2.5Mn (mass%) model Mo_2NiB_2 complex boride base hard alloys with four levels of Mo contents corresponding to Mo/B atomic ratio ranging from 1.0 to 1.3 were prepared to study the effects of the Mo/B atomic ratio on the mechanical properties and the microstructure. A strong correlation between the mechanical properties and the phase formation was observed in the hard alloys.

TRS increased with increasing Mo/B atomic ratio and showed a maximum value of 3.25 GPa at the Mo/B atomic ratio of 1.2 and then decreased with increasing Mo/B atomic ratio. Hardness increased linearly from 86.8HRA to 90.8HRA with increasing ratio.

The XRD results revealed that the main constituents were the tetragonal Mo_2NiB_2 complex boride and the Ni base binder. The Mo/B atomic ratio of 1.2 higher than the stoichiometric Mo content showed a very fine ideal two-phase structure with homogeneous distribution of the tetragonal Mo_2NiB_2 complex boride in the solution

strengthened Ni base binder and hence exhibited excellent TRS and hardness. On the other hand, the alloy with the low Mo/B atomic ratio of 1.0 contained the orthorhombic Mo_2NiB_2 and the alloy with the high Mo/B atomic ratio of 1.3 included Mo and the V–Mn intermetallic compound in addition to the two major constituents. These three phases degraded the mechanical properties of the alloys.

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