Effect of double addition of V and Cr on the properties of Mo$_2$NiB$_2$ ternary boride-based cermets

Yuusuke Shiota, Yuuta Miyajima, Takuya Fujima and Ken-ichi Takagi
Department of Mechanical Engineering, Tokyo City University
1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan
E-mail: ktakagi@tcu.ac.jp

Abstract. The effect of double addition of V and Cr on the mechanical properties and microstructure of Mo$_2$NiB$_2$ base cermet was investigated. Total additional amount of V and Cr was fixed to 12.5 mass% and the fraction between the two additives was varied. Transverse rupture strength (TRS) and Rockwell A-scale hardness (HRA) were measured on the cermets and discussed together with their microstructure obtained by X-ray diffraction (XRD) and backscattered electron images (COMP). Addition of 2.5-mass% Cr and 10-mass% V showed the highest mechanical properties. Microstructural analysis revealed that brittle orthorhombic-M$_3$B$_2$ phase was formed in high V fraction. The corrosion resistance of the cermets against hydrochloric acid was superior to that of JIS SUS 304. The resistance against nitric acid decreased with decreasing Cr content and was lower than that of SUS 304.

1. Introduction
Tungsten carbide based cermets are the most widely used wear resistant hard materials in the world. In spite of its importance for various industries, tungsten ore production is quite uneven across countries, that is, 86% is in China[1]. Reduction of scarce and unevenly distributed resources such as tungsten, indium, cobalt and dysprosium is a recent crucial issue all over the world. Now wear resistant hard material with less or without tungsten is a hot research topic.

Ternary boride-based cermet is a promising candidate as a substitute material for cemented carbides due to its excellent mechanical properties[2]. Transition metal borides show high hardness, high melting point and electrical conductivity, which make the borides suitable for a new wear resistant material.

Although the brittleness of the metal borides requires their practical application to be in a form of cermet materials in which the borides are used as hard phase, high chemical reactivity of the borides forms a new brittle phase between the hard phase and metallic binder phase. Because of these characteristics, it was difficult to develop cermets with a hard boride phase. A recently developed technique, Reaction Boronizing Sintering, has realized the new type of boride base cermet[3]. Cermets with Mo$_2$FeB$_2$ and Mo$_2$NiB$_2$ for its hard phase, ternary boride-based cermets, have been developed by this methodology and are now commercially available.

The Mo$_2$NiB$_2$ cermet shows lower mechanical properties and higher corrosion resistance by using Ni for base metal in comparison with Mo$_2$FeB$_2$ cermet. Mo$_2$NiB$_2$ takes the orthorhombic-M$_3$B$_2$ type crystal structure (here, M stands for metallic element), which causes its grain growth in the plate-like shape during sintering and brittleness for the bulk material.
Table 1. Chemical composition of sample cermets. Nickel balances the total fraction for all the cermets.

| Cermet | B  | Mo | Cr | V  | Ni   |
|--------|----|----|----|----|------|
| A      | 6.0| 55.9| 7.5| 5.0| bal. |
| B      | 6.0| 55.9| 5.0| 7.5| bal. |
| C      | 6.0| 55.9| 2.5| 10.0| bal. |
| D      | 6.0| 55.9| 0.0| 12.5| bal. |

It is known that the addition of some amount of chromium (Cr) or vanadium (V) into Mo$_2$NiB$_2$ changes its crystalline structure to tetragonal-M$_3$B$_2$ type, which leads to microstructural refinement and improved mechanical properties of Mo$_2$NiB$_2$ cermet[2, 4]. The V-added cermet exhibits finer boride grain within it and better mechanical properties. The Cr-added cermet, on the other hand, realizes better corrosion resistance by forming an insulating passivation layer on its surface. Addition of both V and Cr into Mo$_2$NiB$_2$ cermets has a prospect of coincident realization of good mechanical properties and corrosion resistance.

We, therefore, investigated the mechanical properties, corrosion resistance and microstructure of the V-Cr double added Mo$_2$NiB$_2$ cermet in this study. The amount of added V and Cr was fixed to 12.5 mass% in total and the their fraction dependence was investigated since the both single addition of V or Cr showed maximal mechanical properties at 12.5 mass% addition in previous studies[4] and they were indicated to replace the same site in the boride crystal: Ni site.

2. Experimental procedure

Table 1 shows the chemical composition of the cermets we prepared. Content of Cr was varied from 0.0 up to 7.5 mass% with trading off that of V to keep their total content as 12.5 mass%.

All the samples were made from following powders: carbonyl nickel (99.85 %), pure Mo (99.95 %), MoB (Mo: 89.52 %, B: 10.26 %), VB$_2$ (V: 68.93 %, B: 29.84 %) and CrB (Cr: 82.99 %, B: 16.54 %). We also added 0.35 mass% of graphite to reduce oxide within the samples by chemical reaction during the sintering. The mixed powders were ball-milled in acetone to reduce the average particle size to about 1µm.

The powder mixtures were dried in vacuum at 50 °C for 12 hours then pressed under a pressure of 98 N/mm$^2$ to form green compacts. They were sintered in vacuum for 30 min. at 1473 and 1523K.

Rockwell A-scale hardness (HRA) and transverse rupture strength (TRS) measurements were performed on the sintered compacts. We used test specimens with dimension of 4.0 x 8.0 x 25.0 mm for the TRS bending in three point loading mode with 20 mm span. X-ray diffraction (XRD) and backscattered electron images (COMP) were used for the study of the microstructure of the cermets. We used RAD-rR (Rigaku Co. Ltd.) with Cu-Kα for XRD, and JXA-8200 (JEOL) for COMP images.

The corrosion resistance was investigated for the specimens sintered at 1523K by measuring their corrosion weight loss after soaking in the 10 wt% hydrochloric acid (HCl) and nitric acid (HNO$_3$) at 50 °C for 20 hours. The specimens used for this test had dimensions of 4.0 x 8.0 x 9.0 mm. A stainless steel, JIS SUS 304 (AISI 304 equivalent), was used for comparison.
3. Results and discussion

As shown in figure 1, HRA exhibits high hardness across all the V and Cr content taking a maximum at 10 mass\% of V and 2.5 mass\% of Cr. The similar tendency is observed for TRS in figure 2. The cermet sintered at higher temperature (1523 K) shows lower hardness but comparable TRS in comparison with the cermet sintered at lower temperature (1473 K). This indicates overgrowth of the boride grains that surely reduces the hardness but has less impact on TRS.

Figure 3 shows XRD patterns for the cermets sintered at 1523 K. The figure indicates that the main constituents of the cermets are tetragonal-M_3B_2 hard boride phase and Ni-based binder. All the ternary borides have changed their structure from orthorhombic into tetragonal, which improves mechanical properties. In all the cermets except for alloy-A (V: 5.0 \%, Cr: 7.5 \%), small amount of brittle tetragonal-M_5B_3 type ternary boride is also formed.

COMP images (figure 4) fully support the XRD results. The figure shows gray boride phase dispersed in dark Ni base binder. Tetragonal-M_3B_2 type ternary boride formation is indicated in these micrographs because grains are quasi-spherical, other than plate-like shaped orthorhombic-M_3B_2 crystals. The micrographs also show tetragonal-M_5B_3 phase as a lightest part between the grains[5].

XRD and COMP results, however, do not provide any clear evidence for the forming of some weak structure that can cause the reduction of hardness and TRS in high V region. The reduction of mechanical properties in high V region is not due to the formation of brittle tetragonal-M_5B_3 phase. There could be certain change or tendency in their sintering behavior like the contiguity of the particles. It is, therefore, necessary to investigate them further in detail.

These results suggest a trade-off relation of two dependencies on V amount added into the Mo\_2NiB\_2 cermet. That is, strengthening of crystalline structure of borides into tetragonal and formation of some brittle or fragile phase are concurrent. This trade-off can cause the maxima in the mechanical properties.

Figure 5 shows the corrosion weight loss in 10 wt\% (a) HCl and (b) HNO\_3 at 50 °C for 20
Figure 2. Added V/Cr ratio dependence of TRS. Open and filled circles correspond to alloys sintered at 1473 K and 1523 K, respectively.

Figure 3. XRD patterns for the cermets sintered at 1523 K.

hours. All the cermets exhibited obviously higher corrosion resistance than SUS 304 in HCl. Their corrosion weight losses in the acid were about a fiftieth of that for SUS 304. Corrosion in the HNO$_3$, by contraries, obviously depends on the V-additive amount as shown in figure 5(b). That is, higher V-additive amount caused more corrosion weight loss. SUS 304 did not lose its weight in the HNO$_3$.

The corrosion weight loss of the cermets did not depend on the V and Cr content in HCl. Nickel is well known to have good corrosion resistance against nonoxidizing acids like HCl and to remarkably improve the resistance by Mo addition. It would appear that Ni and Mo played main role for the high corrosion resistance against HCl, which also resulted in the independence
Figure 4. Microstructure of cermets sintered at 1523 K observed by back scattered electron image (COMP).

Figure 5. Corrosion weight loss against (a) hydrochloric acid in logarithmic scale and (b) nitric acid in linear scale. All the corrosion tests were carried out in 10 wt% acids at 50 °C for 20 hours.
of the corrosion weight loss from the V and Cr additive amount.

The cermets were much more inferior to SUS 304 in the HNO₃. Ni does not have high corrosion resistance against oxidizing acids like HNO₃. Though Cr-passivation layer has high corrosion resistance against the acids, the Cr content was insufficient for stable passivation layer formation in this work. The corrosion resistance, therefore, simply depended on the Cr content.

4. Conclusion
Mo₂NiB₂ cermet with 12.5 mass% of V and Cr addition was investigated for its mechanical properties and microstructure. TRS and hardness showed maxima at an addition of 10 mass% of V and 2.5 mass% of Cr. Though XRD revealed the formation of hard tetragonal-M₃B₂ that improved mechanical properties, no obvious mechanism of its reduction in high V region was found in XRD and COMP results. Further analysis on microstructure and sintering behavior will illustrate composition dependence of mechanical properties. The cermet with V and Cr addition had both high mechanical properties and high corrosion resistance against a nonoxidizing acid. As the corrosion resistance against an oxidizing acid simply depended on the Cr content, adequate balance between mechanical properties and corrosion resistance is to be selected for practical use.

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