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High-Strength Boride Base Hard Materials

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A previous investigation revealed that the addition of Cr to the Mo_2NiB_2 complex boride base cermet changed the boride phase structure from orthorhombic to tetragonal and resulted in the remarkable improvement of mechanical properties and microstructural refinement. In this investigation, the effects of eight alloying elements, such as V, Fe, Co, Ti, Mn, Zr, Nb, and W, on the mechanical properties and microstructure of the cermets were studied by using model cermets with composition of Ni–6 masss% B–58. 6 mass% Mo–10 mass% *X* (*X* = additional elements). From these elements V showed the same effects as Cr showed on the mechanical properties and microstructure associated with a simultaneous phase transformation of the complex boride. Addition of other alloying elements (Fe, Co, Ti, Mn, Zr, Nb, and W) did not exhibit the structural change and strengthening. These elements tended to form coarse grained orthorhombic complex boride, as well as coarse grained carbide or intermetallic compounds which degraded the strength of the cermets. The phase transformation of the Mo_2NiB_2-type complex boride from orthorhombic to tetragonal with optimal addition of Cr and V was essential for the improvement of the mechanical properties and microstructural refinement of the cermet. © 1997 Academic Press

INTRODUCTION

A recently developed novel sintering technique, named reaction boronizing sintering, realized the potential utilities of the outstanding characteristics of the metal borides as ternary boride base cermets with full density and excellent mechanical properties and wear and corrosion resistances (1). These cermets were based on Mo_2FeB_2, Mo_2NiB_2, and WCoB. The Mo_2NiB_2 cermets are formed from a Mo_2NiB_2-type complex boride as a hard phase and a Ni base binder. According to a previous investigation the addition of Cr to the cermet changed the boride phase structure from orthorhombic to tetragonal and resulted in the remarkable improvement of mechanical properties such as transverse rupture strength and hardness and microstructural refinement (2).

In this investigation, the effects of eight alloying elements were studied by using the model cermet with the composition of Ni–6 mass% B–58.6 mass% Mo–10 mass% *X* (*X* = V, Fe, Co, Ti, Mn, Zr, Nb, and W). Since V showed the same response as Cr to the mechanical properties associated with the crystal structural change of the boride, the effect of various V contents on the microstructure and the mechanical properties of the cermet was studied more precisely.

EXPERIMENTAL PROCEDURE

The Ni–6 mass% B–58.6 mass% Mo cermet was used as a standard in this investigation. Eight useful alloying elements for the hard materials, V, Fe, Co, Ti, Mn, Zr, Nb, and W, were selected. Previous work (2, 3) has shown that the maximum transverse rupture strength was achieved with an addition of 10 mass% Cr. Consequently, a composition Ni–6 mass% B–58.6 mass% Mo–10 mass% *X* (*X* = Cr, V, Fe, Co, Ti, Mn, Zr, Nb, and W) was selected in the first part of the present work. In the second part six levels of V from 0 to 12.5 mass% at an interval of 2.5 mass% were added to the standard composition to study the effects of vanadium addition more precisely. The powder mixtures prepared from pure Mo, carbonyl Ni, carbonyl Fe, pure Cr, pure Co, pure Mn, pure W, MoB, VB_2, TiB_2, ZrB_2, and NbB_2 were ball-milled in acetone to an average particle size of about 1 μm. After the mixtures were milled and dried they were pressed to the green compacts which were sintered in vacuum for 1.2 ks at 1493 to 1593 K. To reduce the oxide on the powders an addition of 0.5 mass% graphite as a sintering aid was used. Transverse rupture strength (TRS) and Rockwell "A" hardness of the sintered compacts were measured. The TRS tests were conducted on $4.0 \times 8.0 \times 25$ mm test bars (finished-ground with a No. 170 borazon wheel) which were broken in three point loading with a 20.0 mm span. Five specimens were tested for each composition. The microstructure of the cermets was studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and scanning Auger electron spectroscopy (AES).

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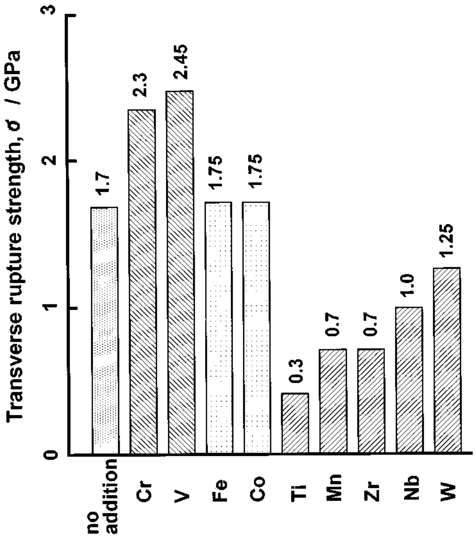

FIG. 1. Transverse rupture strength of Ni–6 mass% B–58.6 mass% Mo–10 mass% X (X, additional element) cermets.

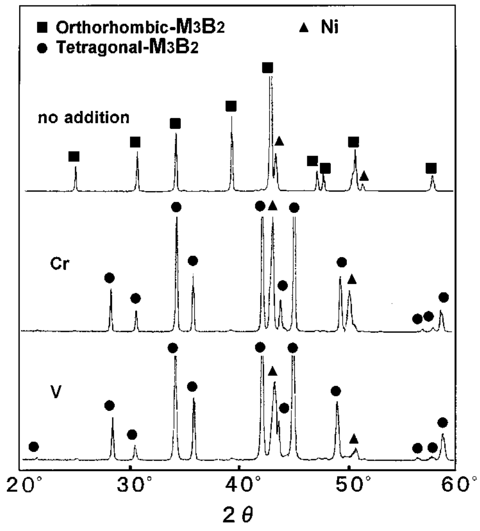

FIG. 3. Cu$K\alpha$ X-ray diffraction patterns of Ni–6 mass% B–58.6 mass% Mo–10 mass% (Cr and V) cermets.

RESULTS

A. The Cermets with Various Alloying Elements: Ni–6 mass% B–58.6 mass% Mo–10 mass% X

(1) Mechanical properties. Figure 1 shows the transverse rupture strength (TRS) of the cermets with addition of 10 mass% of nine alloying elements including Cr. This figure indicates that the results obtained can be divided into three groups. The first group is cermets with Cr and V exhibiting maximum TRS values which are about 0.6 GPa higher than those for the standard composition (no additional alloying element). The second group is Fe and Co containing cermets which have almost the same TRS as the standard one. The third group is cermets with the alloying elements Ti, Mn, Zr, Nb, and W which show drastically reduced TRS. Furthermore it should be noted that all additional elements with the exception of Ti and Mn increase the hardness of the cermet as shown in Fig. 2.

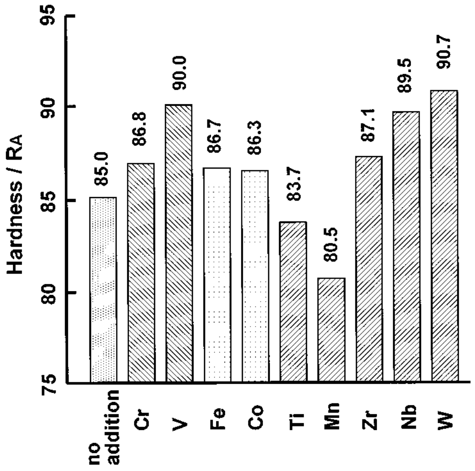

FIG. 2. Rockwell "A" hardness of Ni–6 mass% B–58.6 mass% Mo–10 mass% X (X, additional element) cermets.

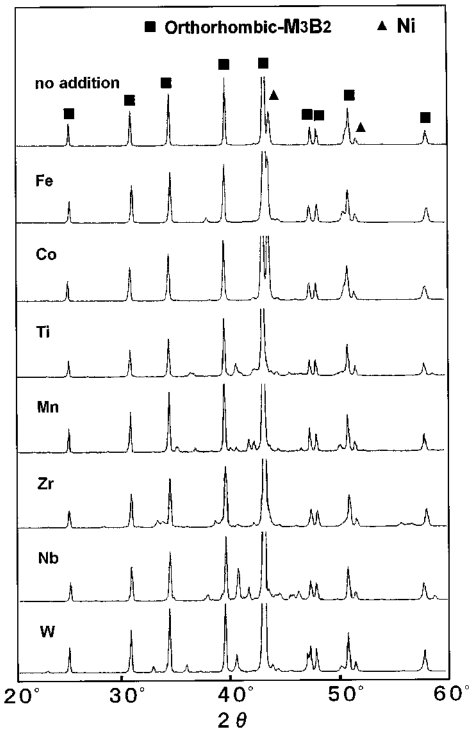

FIG. 4. Cu$K\alpha$ X-ray diffraction patterns of Ni–6 mass% B–58.6 mass% Mo–10 mass% (Fe, Co, Ti, Mn, Zr, Nb, and W) cermets.

(2) X-ray diffraction. To study the structure/property relationship X-ray diffraction analysis was performed. X-ray diffraction results of the standard cermet and those with Cr and V additions are shown in Fig. 3. The figure illustrates that an addition of V, as well as Cr, causes a phase transformation of the complex boride from orthorhombic to tetragonal. Furthermore a small shift of Ni reflections to lower Bragg angles is also detected.

Figure 4 shows the X-ray diffraction results of the cermets with the rest of seven elements such as Fe, Co, Ti, Mn, Zr, Nb, and W. These cermets have almost the same or lower TRS than the standard one. In accordance with the standard cermet, the orthorhombic M_3B_2-type complex boride and the Ni base binder are detected in all of these cermets. Few additional peaks, which might be considered to be peaks of intermetallic compounds or carbides, were also detected, but scarcity and overlapping of the peaks retarded the precise identification. Probably the residual carbon in the sintered compacts may have formed some kind of carbides.

Thus, the phase transformation of the complex boride which occurred during sintering in Cr and V added cermets seems to be responsible for the improvement in the mechanical properties of the sintered two-phase material which consists of the orthorhombic M_3B_2-type complex boride as a hard phase, the Ni base binder, and no brittle third phase.

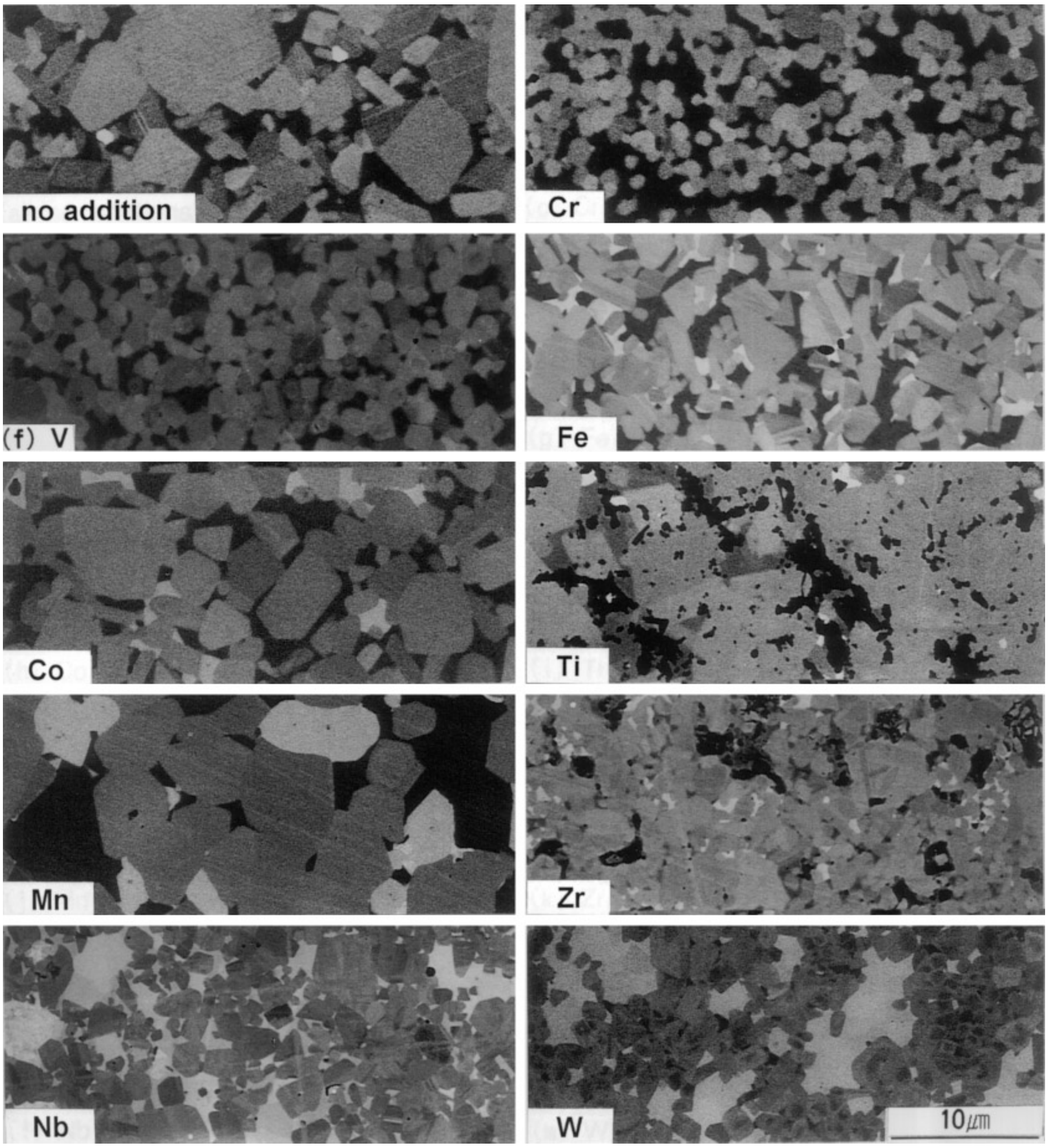

FIG. 5. Back-scattered electron images of Ni–6 mass% B–58.6 mass% Mo–10 mass% X (X, additional element) cermets.

(3) Microstructure. The typical microstructure of the cermets with various additional elements is shown in Fig. 5 using SEM and back-scattered electron images. The coarse rectangular orthorhombic M_3B_2-type complex boride (light gray phase) and the Ni base binder (dark phase) are observable in the micrograph of the standard cermet (no addition). We note that Cr and V added cermets consist of a two-phase structure: (i) fine-grained spherical crystals of the tetragnal M_3B_2 type complex boride and (ii) the Ni base binder. In the case of Fe and Co added cermets small amounts of an unknown third phase (white, not identified by XRD) are observed in addition to the same two main constituents as in the standard cermet. In Ti and Zr added cermets the boride phase becomes coarse-grained, and moreover third phases appear: a dark massive phase in the Ti added cermet and a small white phase in the Zr added cermet. Large boride grains and white particles, which seem to be carbides, are observed in the Mn-containing cermet. In the case of Nb and W addition, boride grains are somewhat coarser and the white third phase locates between the boride grains.

Since carbon analysis of the Ti, Mn, Zr, Nb, and W containing cermets revealed more than 0.2 mass% residual carbon, it seems likely that the unknown third phases in these cermets are carbides. Moreover, it should be noted that residual porosity is observable in Ti and Zr added cermets.

(4) Auger analysis of Cr and V added cermets. The distribution of Cr and V in the cermets was studied by Auger analysis. Auger spectra of four analysis points in the Cr and V added cermets are shown in Fig. 6. In the complex boride (Point 1 and 3) Mo, B, Ni, and a small amount of Cr or V are detected. The binder (Point 2 and 4) contains Mo, Ni, and Cr or V. It is obvious that the elements of Cr and V are present in both the complex boride and the Ni base binder and show almost the same concentration. From the Auger

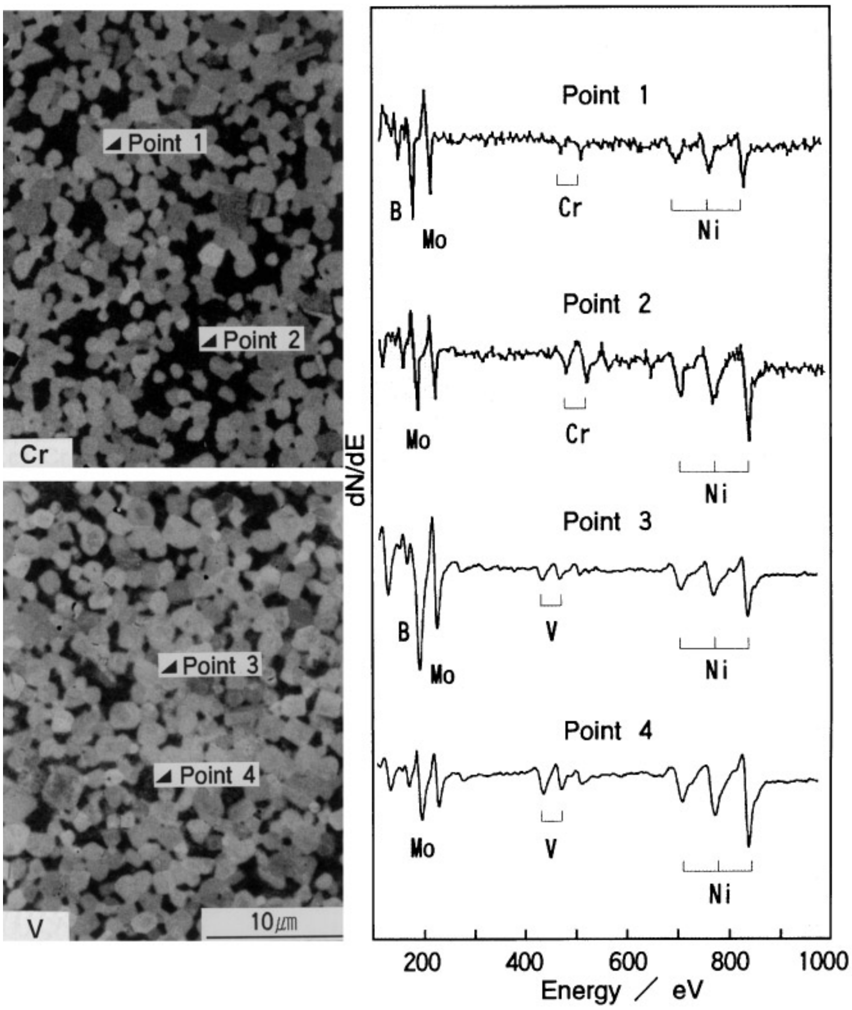

FIG. 6. Back-scattered electron images and Auger spectra of Ni–6 mass% B–58. 6 mass% Mo–10 mass% (Cr and V) cermets.

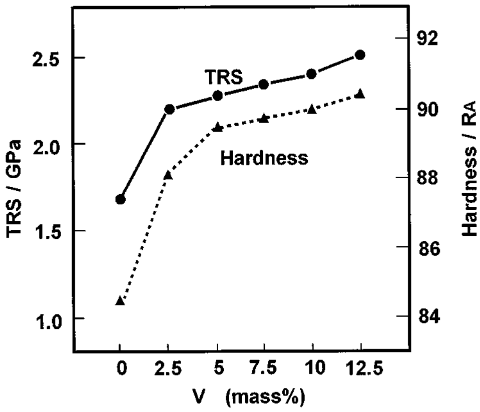

FIG. 7. Transverse rupture strength and hardness of Ni–6 mass% B–58.6 mass% Mo–(0–12.5) mass% V cermets as a function of V content.

spectra we believe that the content of both elements in the binder is a little larger than that in the boride.

Auger analysis of other elements did not show any specific partitioning tendency (presence of elements; only in the complex boride, in the binder, or in both the boride and the binder).

B. Cermets with Various V Content: Ni–6 mass% B–58.6 mass% Mo–(0–12.5) mass% V

In the second part of this work six levels of vanadium from 0 to 12.5 mass% (at a interval of 2.5 mass%) were added to the standard cermet Ni–6 mass% B–58.6 mass% Mo to study the effects of V addition more precisely.

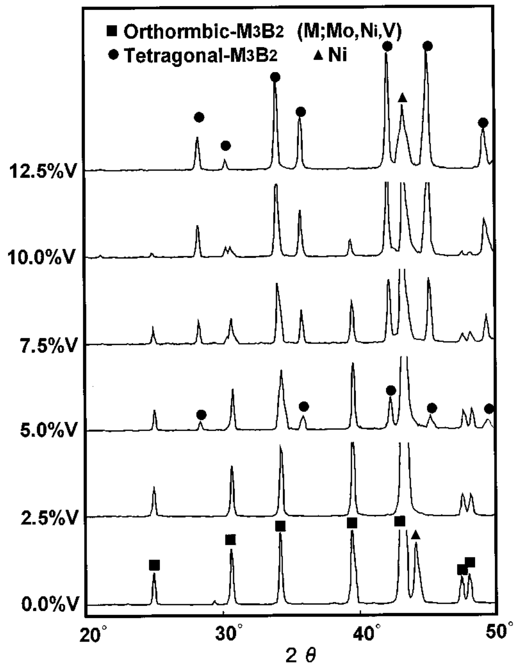

FIG. 8. Cu$K\alpha$ X-ray diffraction patterns of Ni–6 mass% B–58.6 mass% Mo–(0–12.5) mass% V cermets.

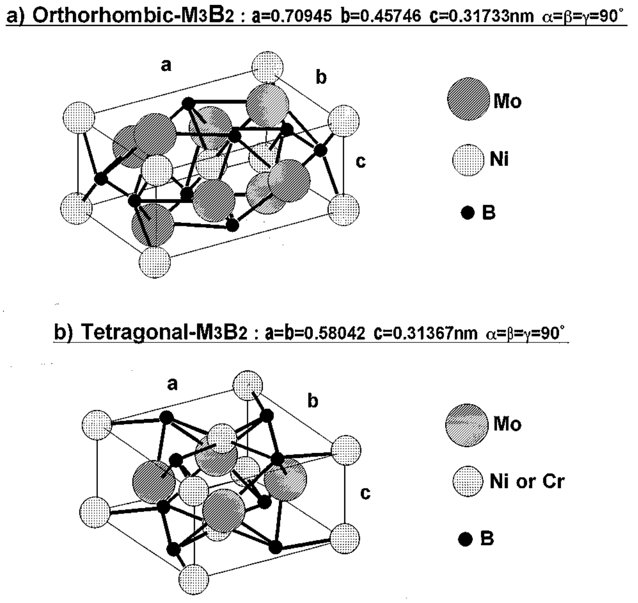

FIG. 9. Orthorhombic (a) and tetragonal (b) unit cells observed in Ni–6 mass% B–58.6 mass% Mo–(0 and 10) mass% Cr cermets.

(1) Mechanical properties. As shown in Fig. 7 both TRS and hardness increase with increasing V content and reach the maxima of 2.5 GPa and 90.5 RA at 12.5 mass% V. It should be noted that even 2.5 mass% V addition drastically increases both TRS and hardness.

(2) X-ray diffraction. Figure 8 summarizes the X-ray diffraction results of V added cermets. The orthorhombic M_3B_2-type complex boride and the Ni base binder are detected in nil and 2.5 mass% V added cermets. The addition of V induces a shift of the Ni reflections to lower Bragg angles which is not observed in the non-V cermet. In the cermet with 5 mass% V, another phase, namely a tetragonal

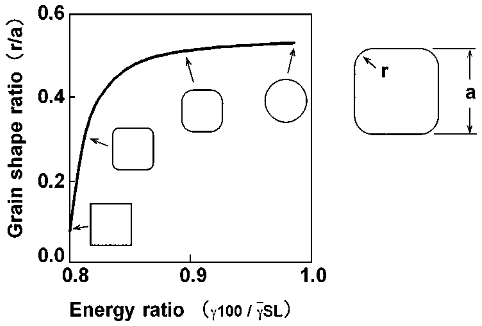

FIG. 10. The grain shape ratio as a function of the energy ratio of the solid–liquid interfacial energy for {100} plane divided by the mean surface energy (after 4).

M_3B_2-type complex boride is observed. The amount of the tetragonal M_3B_2 phase increases with increasing V content of the cermets. Finally at 12.5 mass% V the orthorhombic M_3B_2 phase disappears and only tetragonal M_3B_2 and the Ni base binder are detected.

DISCUSSION

To study the microstructure/property relationship in advanced hard materials, it is very important to investigate the fracture origin on the fracture surface in the case of Cr- and V-containing cermets with very high TRS. No clear fracture origins, so-called “white spots,” were observed on the fracture surface. However, in the cermets with other additional elements, always coarse grains of either the complex borides or carbides, as well as intermetallic compounds, were found in the white spots. Low values of TRS were attributed to these coarse grains of the orthorhombic M_3B_2 phase and the third phases, which act as defects. Standard deviation of TRS values of first group cermets (Cr and V containing cermets) was about 10%. The deviation increased more than that in the order of second group, standard, and third group cermets due to the formation of large fracture origins.

Figure 9 illustrates Reitveld analysis results of the complex boride structures of cermets with and without Cr. By comparison of these structures it is clearly seen that the orthorhombic M_3B_2 structure is more anisotropic than the tetragonal one (3). Figure 10 shows the grain shape ratio as a function of the interface energy ratio given by the $\{100\}$ energy γ_{100} divided by the mean energy γ_{SL} calculated by Warren (4). The equilibrium grain shape for a given energy ratio is given by those r/a values which give a minimum value to the interface energy per unit volume assuming no planes besides $\{100\}$ have energies significantly lower than the mean. These results suggest that the grain shape change from near-spherical to perfect cubic takes place by a small decrease in the degree of crystallographic isotropy through anisotropic surface energy. The change from the spherical grain shape to the rectangular one in the M_3B_2-type boride also corresponds to a decrease in isotropy of the crystal structure, which is in good agreement with Warren’s results. Moreover, the tetragonal M_3B_2 boride provides a smaller grain size and hence can be preferable to the orthorhombic M_3B_2 in terms of mechanical properties. The high TRS of the Cr- and V-containing cermets is further attributed to the homogeneous distribution of the tetragonal M_3B_2 boride phase and the absence of third phases. From these results it is believed that the formation of the tetragonal M_3B_2 is indispensable to obtain high strength.

CONCLUSIONS

1. An optimum amount of Cr and V addition to Mo_2NiB_2 complex boride base cermets resulted in the improvement of mechanical properties associated with a simultaneous phase transformation of complex boride from orthorhombic to tetragonal.
2. Addition of other alloying elements such as Fe, Co, Ti, Mn, Zr, Nb, and W did not cause the structural change of the boride. These elements tended to form either coarse grained orthorhombic complex borides or coarse grained carbides and intermetallic compounds which degraded the mechanical properties of the cermets.
3. Concerning the mechanical properties the new cermets based on the tetragonal M_3B_2 boride are superior to the cermets based on the orthorhombic M_3B_2 boride due to the higher degree of isotropy of the tetragonal boride phase, finer grain size of the tetragonal boride phase, and their better microstructural homogeneity.

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