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Effects of Mo/B Atomic Ratio on the Mechanical Properties and Structure of Mo_2NiB_2 Boride Base Cermets with Cr and V Additions

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The effects of Mo/B atomic ratio ranging from 0.8 to 1.5 (Mo contents) on mechanical properties and phase formation were studied for cermets with the composition of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%). A strong correlation between mechanical properties and phase formation was observed in the cermets. The cermets with somewhat higher stoichiometric Mo content, i.e., Mo/ B ratios of 1.1 and 1.2, showed a very fine ideal two-phase microstructure with a homogeneous distribution of a tetragonal Mo_2NiB_2 (M_3B_2)-type complex boride in a solution-strengthened Ni base binder and hence exhibited an excellent transverse rupture strength (TRS) of more than 2.7 GPa and hardness of about 88 R_A. In the cermets with low and high Mo/B ratios, another type of a complex boride, which was an orthorhombic M_3B_2 or a tetragonal M_5B_3 boride, was detected and was considered to deteriorate TRS due to a coarse-grained microstructure. © 2000 Academic Press

Key Words: **boride base cermet; Mo_2NiB_2 ternary boride; mechanical properties; phase formation; X-ray diffraction.**

INTRODUCTION

In the past decade several ternary boride base cermets became commercially available and have successfully found applications to various wear-resistant materials such as injection molding machine parts (1). Mo_2NiB_2 base cermets consist of a Mo_2NiB_2-type complex boride as a hard phase and a Ni base binder. The cermets have excellent mechanical properties such as high hardness, high transverse rupture strength (TRS), and excellent corrosion and heat resistance. Additions of either or both of Cr and V to the cermet changed the boride phase structure from orthorhombic to tetragonal and resulted in remarkable improvements of mechanical properties such as TRS and hardness and microstructural refinement (2, 3). Mo is one of the main constituents to form the Mo_2NiB_2 ternary boride in the cermets. Previous investigations (3, 4) revealed that Mo was distributed not only in the ternary boride but also in the Ni base binder. This paper focuses on the effect of Mo/B atomic ratio ranging from 0.8 to 1.5 (Mo contents) on the mechanical properties and the phase formation in the cermets with model compositions containing Cr and V.

EXPERIMENTAL PROCEDURE

The compositions of powder mixtures of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%) model cermets with eight levels of Mo/B atomic ratio ranging from 0.8 to 1.5 are given in Table 1.

The powder mixtures prepared from VB_2 (Japan New Metals, mean particle size, 3.13 μm), carbonyl Ni (INCO; type 123, 99.75%, mean particle size, 3–7 μm), pure Mo (Japan New Metals; 99.9%, mean particle size, 1.53 μm), and pure Cr (Nichiju New Material; 99.8%, − 200 mesh) were ball-milled in acetone to an average particle size of about 1 μm. A same kind of boride base cermet balls was used for ball milling. The wear of the balls was very slight and negligible due to their similar composition to the investigated model cermets. After milling and drying the mixtures were pressed to green compacts which were sintered in vacuum for 1.2 ks at 1513 to 1613 K. To reduce the oxide content of the powders 0.5 wt% graphite was added as a sintering aid. Transverse rupture strength and Rockwell "A" hardness of the sintered compacts were measured. The TRS tests were conducted on 4.0 by 8.0 by 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).

RESULTS

A. Mechanical Properties

Figure 1 shows the transverse rupture strength of the model cermets with the Mo/B atomic ratios of 0.8, 1.0, 1.2,

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TABLE 1
Compositions of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%) Model Cermets

Cermet	Mo/B atomic ratio	B	Mo	Cr	V	Ni
A	0.8	5.0	35.6	3.5	11.5	Bal.
B	0.9	5.0	40.0	3.5	11.5	Bal.
C	1.0	5.0	44.4	3.5	11.5	Bal.
D	1.1	5.0	48.8	3.5	11.5	Bal.
E	1.2	5.0	53.2	3.5	11.5	Bal.
F	1.3	5.0	57.6	3.5	11.5	Bal.
G	1.4	5.0	62.0	3.5	11.5	Bal.
H	1.5	5.0	66.4	3.5	11.5	Bal.

and 1.4 as a function of sintering temperature. The optimum sintering temperature where the maximum TRS is obtained for each Mo/B ratio increases with increasing Mo/B ratio.

Figure 2 shows the maximum TRS together with hardness of the model cermets at the optimum sintering temperature as a function of Mo/B atomic ratio. TRS increases up to the Mo/B ratio of 1.2, shows a maximum of 2.95 GPa, and then drops drastically with increasing Mo/B ratio. On the other hand, hardness raises monotonically up to the value of 89.6 R_A at 1.3 Mo/B and then slightly increases to 90.5 R_A at 1.5 Mo/B ratio. These results indicate that both the TRS and the hardness of the cermets depend strongly on their Mo/B ratio.

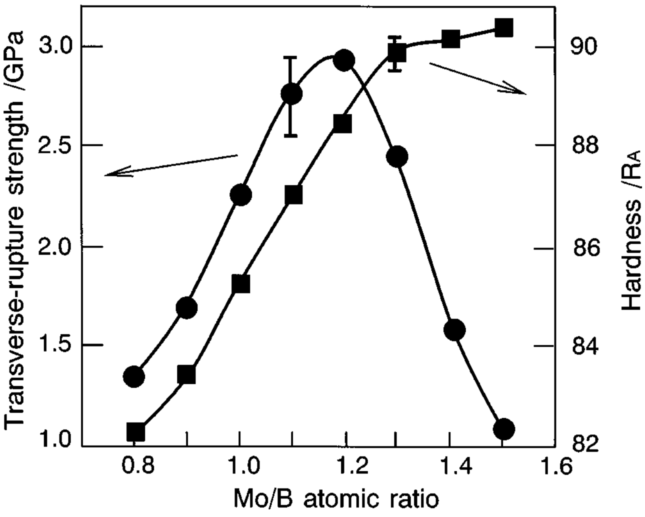

FIG. 2. Transverse rupture strength and hardness of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%) model cermets as a function of Mo/B atomic ratio.

Densities of the model cermets at the optimum sintering temperature were shown in Fig. 3 as a function of Mo/B ratio. The density increase with Mo/B ratio is associated with the increase in heavy molybdenum.

B. X-ray Diffraction

The structure/property relationship of the cermets was studied by X-ray diffraction analysis. The diffraction results of the cermets with the Mo/B ratios of 0.8, 1.0, 1.2, and 1.4

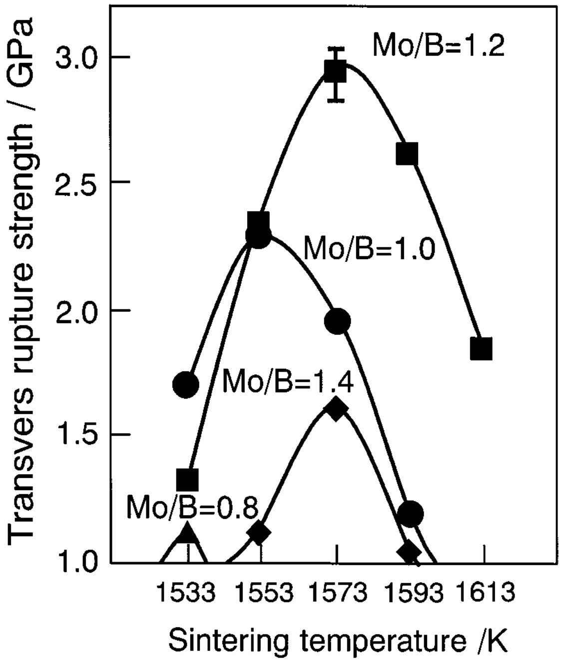

FIG. 1. TRS of Ni–5B–*x*Mo–3.5Cr–11.5V (wt%) cermets as a function of sintering temperature (sintering time, 1.2 ks).

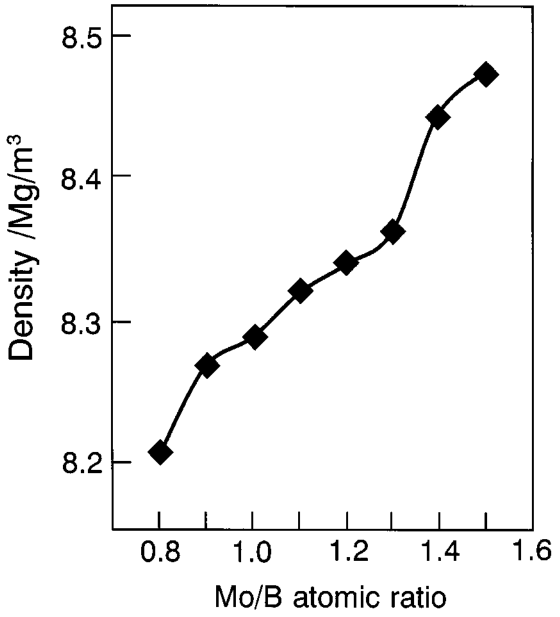

FIG. 3. Density at the optimum sintering temperarure of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%) model cermets as a function of Mo/B atomic ratio.

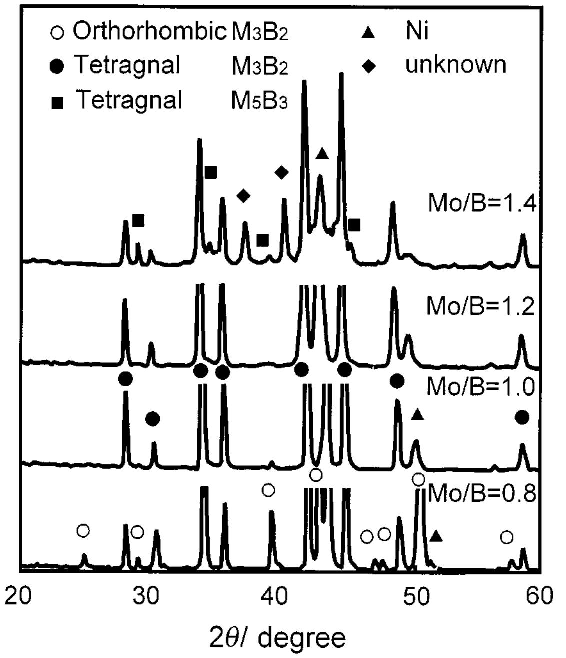

FIG. 4. Cu*K*α X-ray diffraction patterns of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%) model cermets.

TABLE 2
X-ray Diffraction Results of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%) Model Cermets

Cermet	Mo/B ratio	Orthorhombic M_3B_2	Tetragonal M_3B_2	Tetragonal M_5B_3	Ni	unknown
A	0.8	S	VS		S	
B	0.9	M	VS		S	
C	1.0	VW	VS		S	
D	1.1		VS		S	
E	1.2		VS		S	
F	1.3		VS	W	S	W
G	1.4		VS	M	M	M
H	1.5		VS	W	W	S

Note. S, strong; M, medium; W, weak; V, very.

are shown in Fig. 4. Table 2 summarizes the phases identified by XRD in the cermets.

The table and figure indicate that all of the cermets contain the two main constituents of the Mo_2NiB_2 (M_3B_2) complex boride with the tetragonal structure and the Ni base binder. Besides the two main constituents the cermets

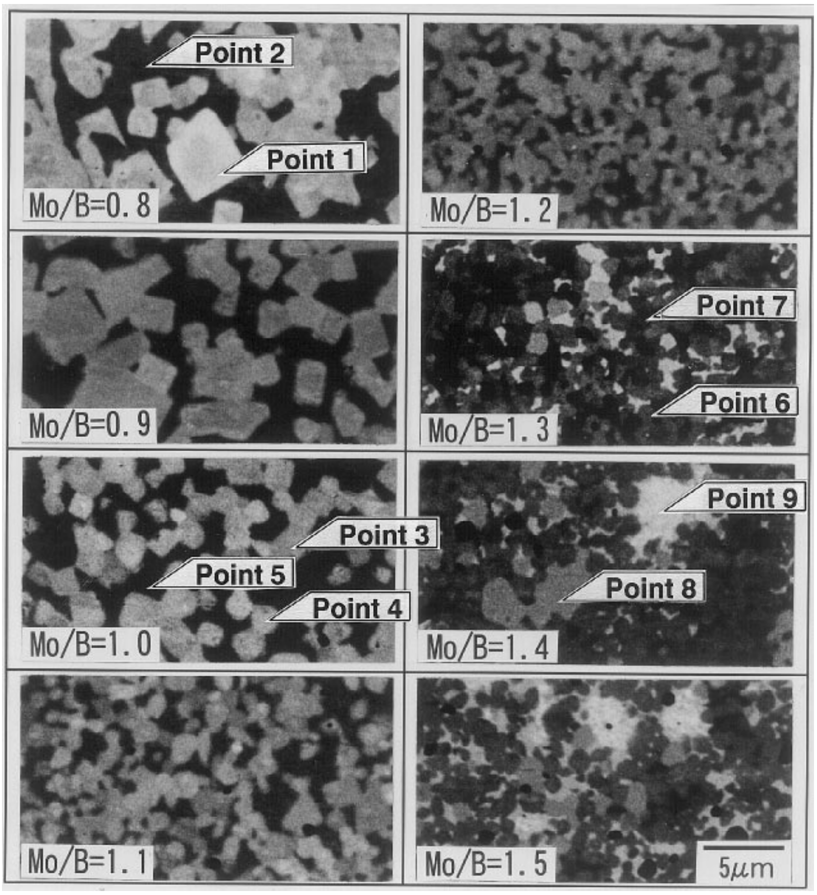

FIG. 5. Backscattered electron images of Ni–5B–*x*Mo–11.5V–3.5Cr cermets sintered at the temperature where the maximum TRS was obtained for each Mo/B ratio.

with low Mo/B ratios from 0.8 to 1.0 contain the orthorhombic Mo_2NiB_2 (M_3B_2), whose amount decreases with increasing Mo/B ratio. The cermets with medium Mo/B ratios of 1.1 and 1.2, i.e., with somewhat higher stoichiometric Mo content, exhibit an ideal two-phase structure of the tetragonal M_3B_2 boride and the Ni base binder. The cermets with high Mo/B ratio consist of a tetragonal M_5B_3 and an unknown phase in addition to the two main constituents. The amount of the unknown phase increases with increasing Mo/B ratio.

C. Microstructure

Figure 5 shows the microstructure of the model cermets investigated by backscattered electron images (BEIs) and nine Auger analyzed points. Corresponding Auger spectra are shown in Fig. 6. In the BEI images the Ni base binder appears dark and the complex boride phases appear gray. Cr and V are detected in both the Ni base binder and the boride phases and are enriched in the boride phases. Square-shaped boride grains (points 1 and 3) contain some amount of V and Cr in addition to Mo, B, and Ni. Small round-shaped boride grains (points 4 and 6) also consist of the same elements as the square-shaped ones but contain less Ni. Considering the XRD and Auger analysis results, the square-shaped boride is the orthorhombic M_3B_2 phase and the round-shaped boride is tetragonal M_3B_2. Both of the boride phases are observed in the cermets with Mo/B ratios less than 1.0. At medium Mo/B ratios of 1.1 and 1.2 only the tetragonal M_3B_2 is observed as a boride phase. The grain size of tetragonal M_3B_2 becomes smaller with increasing Mo/B ratio. Above a Mo/B ratio of 1.3 another type of a complex boride and an unknown phase are observed. The grain size of these two phases become large with increasing Mo/B ratio. The light gray particle (point 8) contains Mo, B, V, and Cr, and a minute amount of Ni and is identified as the tetragonal M_5B_3 phase. The white irregular shaped phase (point 9) consists of mainly Mo and a small amount of Cr and V. This phase is considered to be a Mo base alloy. The Auger spectra indicate that the dark phases of points 2, 5, and 7 are the Ni base binder and that the Mo, Cr, and V contents increase and the Ni content decreases with increasing Mo/B ratio. The Ni base binder phase may change from a Ni base solid solution to a Ni–Mo intermetallic compound such as Ni_4Mo and Ni_3Mo associated with increasing Mo/B ratio.

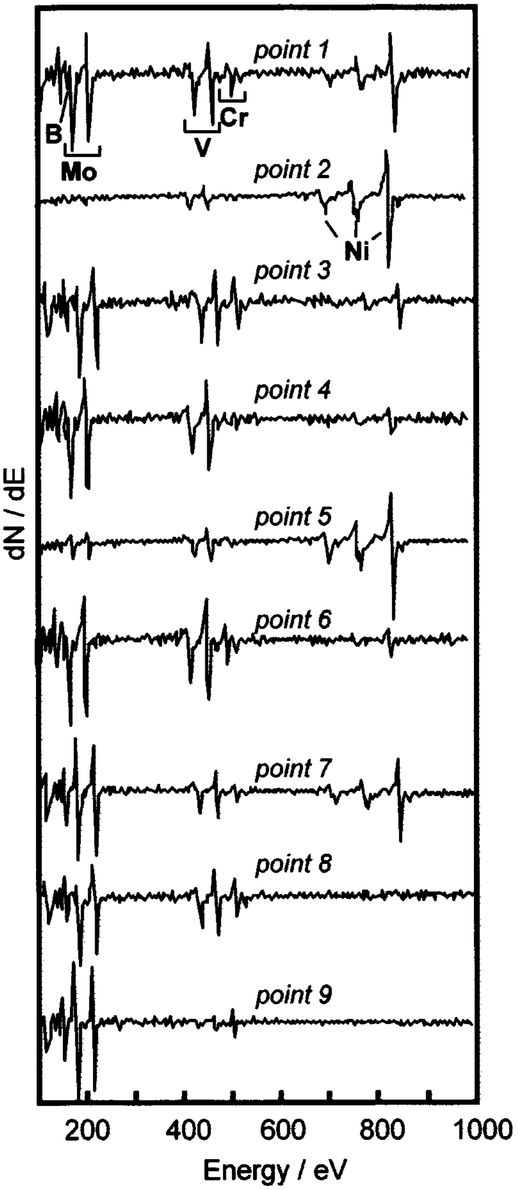

FIG. 6. Auger spectra corresponding to the analysis points indicated on Fig. 5.

DISCUSSION

Studies from the structure/property relationship by XRD, SEM, and AES indicate that the improvement of TRS at low Mo/B ratio is attributable to a decrease in the amount of the orthorhombic M_3B_2 phase and the refinement of the grain size of the complex boride. The solution strengthening of the Ni base binder by the alloying of Mo, Cr, and V plays also an important role for the improvement. The excellent TRS at 1.2 Mo/B is attributed to a very fine ideal two-phase microstructure with homogeneous distribution of the tetragonal M_3B_2 in the solution strengthened Ni base binder. The presence of relatively coarse tetragonal M_5B_3 results in the TRS drop at high Mo/B ratios above 1.3. As shown in Fig. 7 fracture surface investigation reveals that very coarse complex boride grains are observed at the center of the fracture origin at 0.8 and 1.5 Mo/B ratio, while the fracture surface of the specimen at 1.2 Mo/B ratio exhibits fine and uniform boride grains. These fracture results indicate that

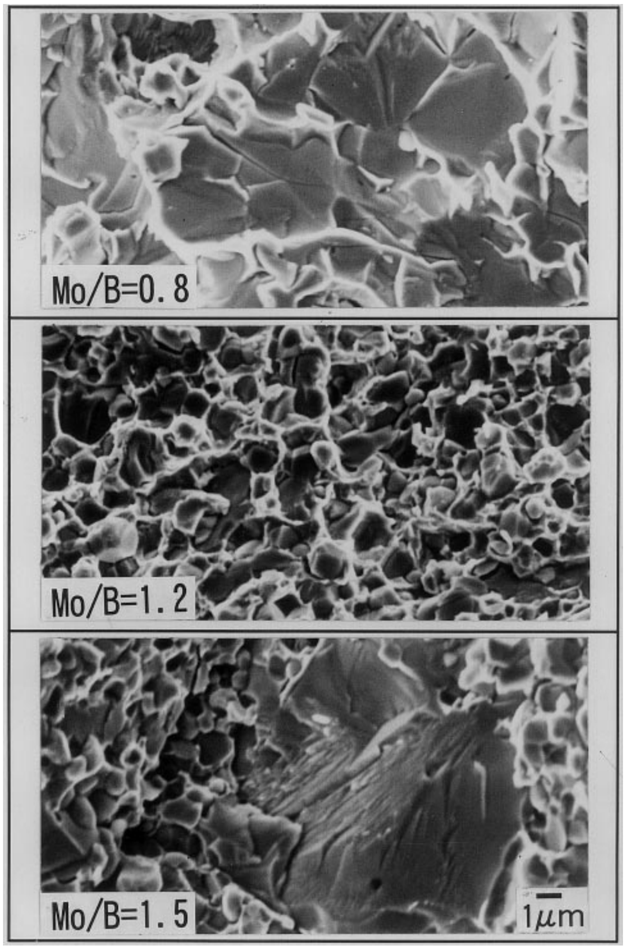

FIG. 7. SEM micrographs of fracture surfaces of Ni–5B–*x*Mo–3.5Cr–11.5V cermets.

coarse grains of the orthorhombic M_3B_2 and the tetragonal M_5B_3 act as a fracture origin and are consistent with the microstructural investigation.

It is very difficult to precisely determine the partitioning of Cr and V in both the boride and the binder phases. Assuming that Cr and V are partitioned equally in the boride and the binder phases the approximate composition region is shown in the isothermal cross section of the Mo–B–Ni ternary system at 1073 K (5) in Fig. 8. This estimated region implies that the hardness increase with increasing Mo/B ratio is attributed not only to the refinement of boride grains and the solution strengthening of the Ni base binder but also to the slight increase of B content, i.e., the increase of the boride phase amount. This figure and Auger spectra also suggest that the Ni base binder phase changes from a Ni base solid solution to Ni-rich intermetallic compounds and then to a Mo base solid solution with increasing Mo/B ratio. Inclination change of hardness at 1.3 Mo/B may correspond to the main constituent change from Ni to Mo in the binder.

A two-phase structure consisting of the tetragonal M_3B_2 and the solution-strengthened Ni base binder and somewhat higher stoichiometric Mo content is indispensable for attaining excellent transverse rupture strength and hardness in the Mo_2NiB_2 ternary boride base cermets.

CONCLUSIONS

The effects of Mo/B atomic ratios ranging from 0.8 to 1.5 on the mechanical properties and the phase formation were studied for cermets with the composition of Ni–5.0B–*x*Mo–3.5Cr–11.5V (wt%). A strong correlation between mechanical properties and phase formation was observed in the cermets.

Transverse rupture strength increased with increasing Mo/B ratio and showed a maximum value of 2.95 GPa at Mo/B = 1.2 and then decreased with increasing ratio. Hardness increased monotonically from $82R_A$ to $89.6R_A$ up to the ratio of 1.3 and then gradually increased to 90.5 R_A at 1.5 Mo/B.

X-ray diffraction results revealed that in addition to the main constituents of the tetragonal Mo_2NiB_2 ternary boride and the Ni base binder the orthorhombic Mo_2NiB_2 was detected at Mo/B ratios of 0.8 to 1.0. The cermets with somewhat higher stoichiometric Mo content, i.e., Mo/B ratio of 1.1 and 1.2, showed a very fine ideal two-phase microstructure with homogeneous distribution of the tetragonal Mo_2NiB_2 (M_3B_2)-type complex boride in the solution-strengthened Ni base binder and hence exhibited excellent TRS and hardness. For the ratio higher than 1.3 another tetragonal M_5B_3-type ternary boride appeared in addition to the two main constituents. The M_5B_3-type boride was considered to deteriorate TRS due to a coarse-grained microstructure. The Ni base binder phase

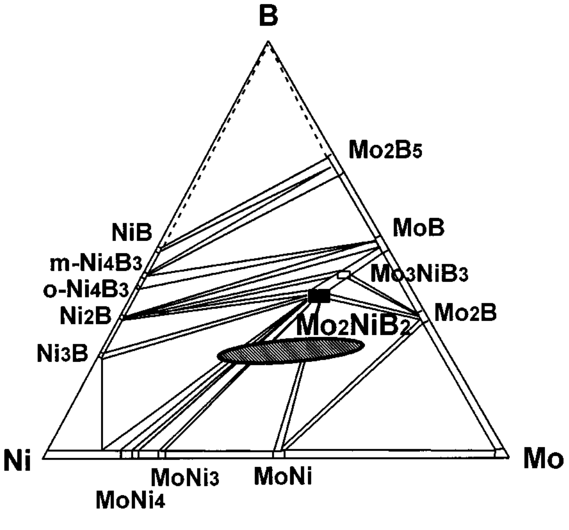

FIG. 8. Isothermal cross section of B–Mo–Ni system at 1073 K (after Yu. B. Kuz'ma and M. V. Chepiga, 1969, *Sov. Powder Met.* **10**(82), 832.

changes from a solid solution to Ni-rich intermetallic compounds and then to a Mo base solid solution with increasing Mo/B ratio. This change also affected the mechanical properties.

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