15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

NOVEL BORIDE BASE CERMETS WITH VERYHIGH STRENGTH

Ken-ichi Takagi, Mari Yonetsu and Yuji Yamasaki

Toyo Kohan Co., Ltd. Kudamatsu, 744-8611 Japan

Summary:

Mo_2NiB_2 boride base cermets consist of a Mo_2NiB_2 type complex boride as a hard phase and a Ni base binder. The addition of Cr and V to the cermets changed the boride structure from orthorhombic to tetragonal and resulted in the improvement of mechanical properties and microstructural refinement. The tetragonal Mo_2NiB_2 was formed through the orthorhombic Mo_2NiB_2 by the solid state reaction during sintering and not formed directly from the raw material powders. Ni-4.5B-46.9Mo-12.5V-xMn (wt%) model cermets with five levels of Mn content from 0 to 10wt% were prepared to investigate the effects of Mn on the mechanical properties and microstructure of Mo_2NiB_2 base cermets. The transverse rupture strength (TRS) of the cermets depended strongly on the microstructure, which varied significantly with Mn content. The maximum TRS obtained at 2.5wt%Mn were 3.5Gpa with hardness of $87R_A$.

Keywords:

Boride base cermet, ternary boride, reaction sintering, Mo_2NiB_2, microstructure, mechanical properties

1. Introduction:

Borides, especially transition metal boride, with exceptional mechanical, chemical, electrical and thermal properties have been explored as promising candidates for high-tech applications, especially wear resistant applications, for many years. However, poor sinterability and extreme brittleness resulted from high degree of covalent bonding in the borides and strong chemical reaction between a boride and a metal matrix have limited production of bulk

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

materials in structural component geometry. Recently a novel sintering technique has been developed for liquid phase sintering of boride base cermets associated with the in-situ reaction formation of ternary borides in a metal matrix. This new sintering technique, named "*reaction boronizing sintering*" (1), has already developed three ternary boride base cermets such as Mo_2FeB_2 (2), Mo_2NiB_2 (3) and WCoB (4) base ones. These new cermets, especially Mo_2FeB_2 base one, have been successfully applied to wear resistant applications such as injection molding machine parts, can making tools, hot copper extruding dies, etc. due to their unique properties such as less aggression to mating materials in sliding wear, capability to diffusion- and sinter-bonding to steel and excellent corrosion resistance (1).

The Mo_2NiB_2 boride base cermet consists of a Mo_2NiB_2 type complex boride (5) as a hard phase and a Ni base binder. Previous investigations revealed that the addition of Cr and V to the cermets changed the boride structure from orthorhombic to tetragonal and resulted in the improvement of mechanical properties and microstructural refinement (3, 6, 7). Moreover, an addition of Mn significantly improved the mechanical properties of the cermets. This paper summarizes the sintering behaviour of the Cr and V containing cermets (8) and focuses on the effects of Mn addition on the mechanical properties and microstructure of the Mo_2NiB_2 base cermets.

2. Cr and V added Mo_2NiB_2 boride base cermets:

From the previous investigations the addition of Cr and V to the Mo_2NiB_2 base cermets changed the ternary boride structure from orthorhombic to tetragonal and resulted in the remarkable improvement of mechanical properties such as transverse rupture strength (TRS) and hardness and microstructural refinement (6). Table 1 shows the compositions of three Mo_2NiB_2 base cermets, which have a basic composition with the orthorhombic boride structure and are 10wt%Cr and 12.5wt%V added ones with the tetragonal structure.

As shown in Fig. 1, Cr and V additions drastically improve TRS and Rockwell "A" hardness of the basic cermets. TRS increases from 1.70 GPa to 2.35 GPa for the Cr added cermet and 2.50 GPa for the V added one. The hardness also increases from $84.5R_A$ to 86.5 and $90.5R_A$, respectively.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

Table 1 Compositions of the Mo_2NiB_2 boride base cermets / wt%

Cermet	B	Mo	Cr	V	Ni
Basic cermet	6.0	58.6	_	_	Balance
Cr added cermet	6.0	58.6	10.0	_	Balance
V added cermet	6.0	58.6	_	12.5	Balance

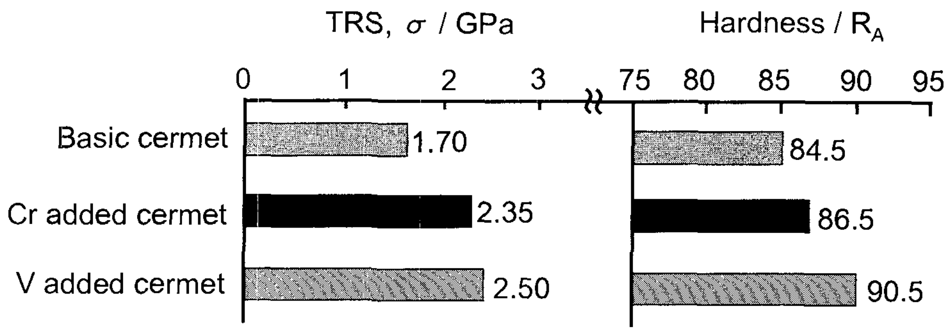

Fig. 1 Transverse rupture strength and hardness of the three Mo_2NiB_2 base cermets

Fig. 2 illustrates the sintering behavior and the ternary boride phase structure formed during sintering of the three cermets. During the solid state sintering stage in the basic cermet the orthorhombic Mo_2NiB_2 was formed in the compact prior to liquid formation by the reaction of 2MoB + Ni = Mo_2NiB_2. During the liquid phase sintering above 1253K, the quasi-eutectic reaction between the orthorhombic Mo_2NiB_2 boride and the Ni base matrix forms an eutectic liquid and considerable densification occurs by the particle rearrangement and the solution/reprecipitation of the Mo_2NiB_2. In the case of the Cr and V added cermets the tetragonal Mo_2NiB_2 was formed through the orthorhombic Mo_2NiB_2 by the solid state reaction and not formed directly from the raw material powders (8). Cr and V seem to stabilize the tetragonal Mo_2NiB_2 in the cermets. The formation of the tetragonal Mo_2NiB_2 is indispensable to obtain excellent mechanical properties in the Mo_2NiB_2 complex boride base cermets.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

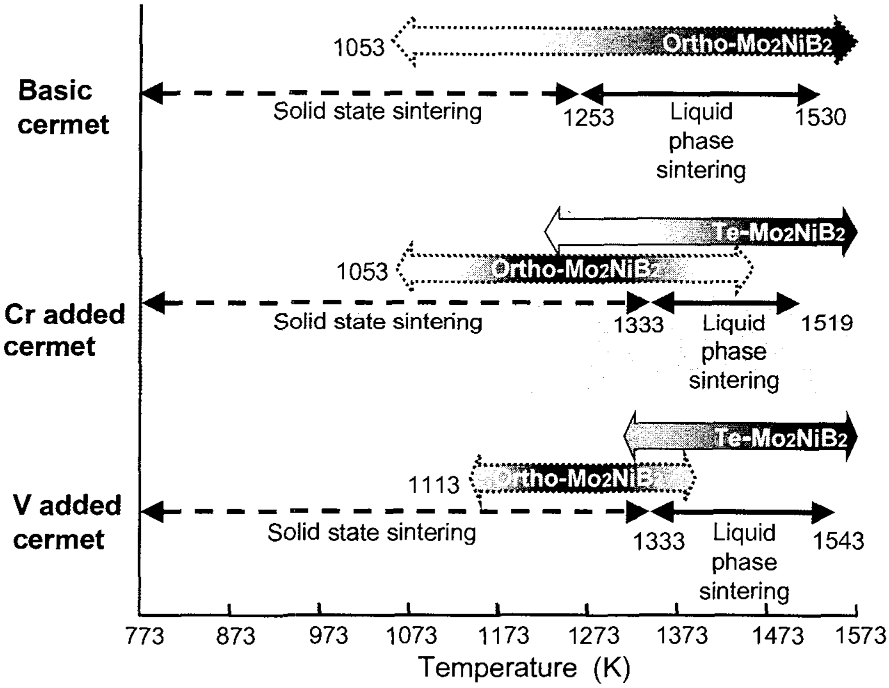

Fig. 2 Schematic illustration of sintering behavior of the three Mo_2NiB_2 base cermets (Ortho-: Orthorhombic, Te-: Tetragonal).

3. Effects of Mn on the properties of the Mo_2NiB_2 boride base cermets:

Our preliminary investigation turned out that the addition of Mn was also effective in improvement of the mechanical properties of the cermets. The effects of Mn on the mechanical properties and microstructure of the cermet were studied using the V added high strength Mo_2NiB_2 boride base one.

3.1 Experimental procedure:

Table 2 shows the composition of Ni-4.5B-46.9Mo-12.5V-xMn (wt%) model cermets with five levels of Mn from 0 to 10wt% used in this investigation.
The powder mixtures prepared from pure Mo, carbonyl Ni, VB and Ni_2B were ball-milled in acetone to an average particle size of about 1μm. After drying,

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

the milled powders were pressed to green compacts and sintered in vacuum for 1.2ks at temperatures between 1533 and 1593K. To reduce the oxides on the powder 0.5wt% of graphite was added as a sintering aid. Transverse rupture strength (TRS) and Rockwell "A" hardness of the cermets were measured. The TRS tests were conducted on 4.0 x 8.0 x 25mm test bars in three point loading with a 20mm span. Five specimens were tested for each composition. The microstructure of the sintered cermets was investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and scanning auger electron spectroscopy (AES).

Table 2 Compositions of the Mn added model cermets / wt%

Cermet	B	Mo	V	Mn	Ni
A	4.5	46.9	12.5	0.0	Balance
B	4.5	46.9	12.5	2.5	Balance
C	4.5	46.9	12.5	5.0	Balance
D	4.5	46.9	12.5	7.5	Balance
E	4.5	46.9	12.5	10.0	Balance

3.2 Phases composing sintered bodies:

X-ray diffraction results indicated that all the Mn added model cermets consisted of the tetragonal Mo_2NiB_2 complex boride and a Ni base binder regardless of Mn content. That is to say, all the cermets maintained original two phase structure and Mn addition did not cause any structural change of the boride phase.

3.3 Mechanical properties:

Fig. 3 shows the maximum TRS together with hardness of the model cermets sintered at optimum temperature where the highest TRS was obtained in each composition as a function of Mn content. TRS reaches a maximum of 3.5Gpa at 2.5wt% and then decreases with increasing Mn content, while the hardness increases linearly up to $88R_A$ at 10wt% Mn.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

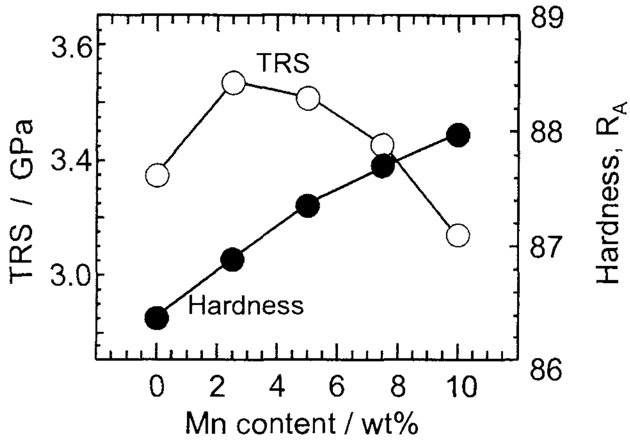

Fig. 3 Transverse rupture strength and hardness of Mn added model cermets as a function of Mn content.

3.4 Microstructure:

Figure 4 shows the back-scattered electron images (BEI) of the model cermets and Auger spectra at nine analysis points. In the BEI images, 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 Mn content, but a part of the Mo_2NiB_2 complex boride exhibits particle coarsening for the 7.5 and 10wt% Mn added cermets.

The partitioning of the alloying elements in the cermets was studied by AES. In the cermet A without Mn , the boride (point 1) contains B, Mo, Ni and V while the Ni base binder (point 2) is alloyed with some amount of Mo and V. In the case of 2.5 to 7.5wt%Mn added cermets B to D having high TRS, the Ni binders (point 4 and 6) also consist of the same elements as the cermet A but the borides (point 3 and 5) contain B, Mo, Ni, V and Mn. In the case of the 10wt%Mn added cermet E showing low TRS, Mn was detected in both the boride (point 7 and 8) and the Ni base binder (point 9). The Mn peak from the small particle (point 7) was higher than that from the large particle (point 8). Mn is dissolved primarily in the Mo_2NiB_2 complex boride for the 2.5 to 7.5wt%Mn cermets, while the 10wt%Mn cermet is dissolved in both the Mo_2NiB_2 complex boride and the Ni base binder.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

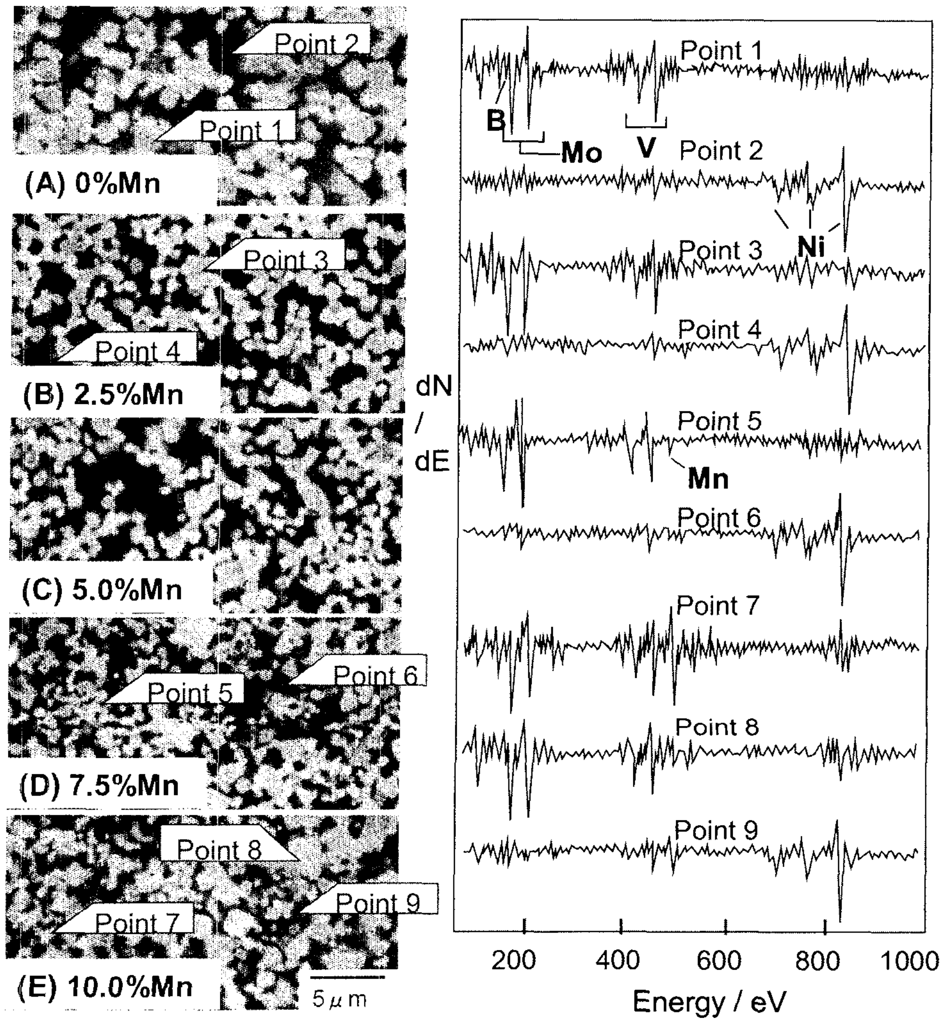

Fig. 4 Back scattered electron images and Auger spectra at nine analysis points of Mn added model cermets.

3.5 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

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

shown in Fig. 5. The mean particle size decreases with increasing Mn content and shows a minimum at 7.5wt%Mn in spite of formation of some coarse particles. It then, increases at 10wt%Mn, because of extensive coarsening. The contiguity of the boride slightly increases up to 5wt%, and further increases for more than 5wt%. High TRS values obtained at 2.5 and 5wt%Mn are attributed to the refinement and uniform distribution of the boride. A very fine, ideal two phase microstructure with homogeneous distribution of the tetragonal Mo_2NiB_2 in the Ni base binder leads to the maximum TRS of 3.5GPa at 2.5wt%. Decrease in TRS for the high Mn containing cermets was caused by increase in contiguity as well as coarsening of some boride particles. Fracture surface investigations revealed that a coarse boride particle was observed at the fracture origin for the 10wt%Mn containing cermet, while the 2.5wt%Mn added cermet showed no distinct fracture origin. Microstructure is significantly changed by an addition of Mn and especially suppression of grain growth of the boride is essential to obtain high strength.

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

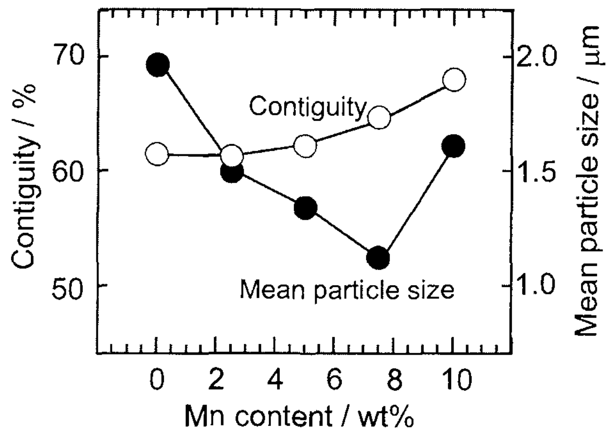

Fig.5 Mean particle size and contiguity of the boride phase in the Mn added model cermets.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

4. Conclusions:

In the Cr and V added Mo_2NiB_2 boride base cermets the tetragonal Mo_2NiB_2 was formed through the orthorhombic Mo_2NiB_2 by the solid state reaction during sintering and not formed directly from the raw material powders. The formation of the tetragonal Mo_2NiB_2 is indispensable to obtain excellent mechanical properties in the Mo_2NiB_2 boride base cermets.
Mn added V containing Mo_2NiB_2 complex boride base cermets consist of the tetragonal Mo_2NiB_2 complex boride alloyed with Mn as the hard phase and the Ni base binder alloyed with Mo and V. Transverse rupture strength increased with increasing Mn content and showed a maximum value of 3.5GPa at 2.5wt% and then decreased with increasing Mn content. Hardness increased monotonically from 86.4R_A to 88.0R_A up to the 10wt%Mn. The high TRS at 2.5wt%Mn was attributed to size refinement and homogeneous distribution of the Mo_2NiB_2 complex boride.

References:

(1) K. Takagi, M. Komai and S. Matsuo: Proc. of 1994 Powder Metallurgy World Congress (PM'94), Vol.1, pp.227-234 (SF2M and EPMA, Les Editions de Physique Les Ulis, France 1994)
(2) K. Takagi, S. Ohira, T. Ide, T. Watanabe and Y. Kondo: Met. Powder Rep., **42** (1987) pp.483-490
(3) M. Komai, Y. Yamasaki, K. Takagi and T. Watanabe: Properties of Emerging P/M Materials, Advances in Powder Metallurgy & Particulate Materials, Vol. 8, pp.81-88 (ed. J. M. Capus and R. M. German, Metal Powder Industries Federation, Princeton, NJ 1992)
(4)M. Komai, Y. Isobe, S. Ozaki and K. Takagi, Proc. of 1993 Powder Metallurgy World Congress, Part 2, pp.1267-1270 (ed. by Y. Bando and K. Kosuge, Japan Society of Powder and Powder Metallurgy, Kyoto, Japan (1993).
(5)Yu. B. Kuz'ma and M. V. Chepiga: Sov. Powder Metall. Met. Ceram. **10** (82) (1969) pp.832-835
(6) K. Takagi, Y. Yamasaki and M. Komai: J. Solid State Chem., **133** (1997) pp.243-248
(7) K. Takagi, Y. Yamasaki and M. Komai: J. Solid State Chem., **154** (2000) pp.263-268
(8) K. Takagi: Mater. Chem. Phys. **67** (2001) pp.214-219