Effect of Mo$_2$C content on the properties of TiC/TiB$_2$ base cermets

Ken-ichi Takagi, Ken Osada, Wataru Koike and Takuya Fujima

Department of Mechanical Engineering, Faculty of Engineering, Musashi Institute of Technology, 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo, 158-8557, Japan

E-mail: ktakagi@sc.musashi-tech.ac.jp

Abstract. The effects of Mo$_2$C content on the microstructure and mechanical properties of TiC/TiB$_2$ base cermets were studied using the model cermets with the compositions of TiC/TiB$_2$-(11-17)Mo$_2$C-24Ni (mass%). TiC and TiB$_2$ ratio is set to molar ratio of 59:41 that is near quasi-eutectic composition. As a result, both transverse rupture strength and hardness of the cermets showed maxima for the cermet containing 13% Mo$_2$C. The cermet achieved remarkable microstructural refinement and still maintained characteristic core-rim structure of the TiC base cermets. TiC/TiB$_2$ cermets, in addition to TiCN base cermets, are a good alternative material to cemented carbides.

1. Introduction
During the last 80 years, WC-Co cemented carbides have been used in various applications such as wear resistant and cutting tool materials. As shown in figure 1 [1], People’s Republic of China holds about 86% of world tungsten mine production. The dependence in the tungsten resources on People’s Republic of China has increased recently. Paucity and uneven distribution of such resources as tungsten, cobalt, etc., have become a crucial issue around the world. Therefore, development of alternative materials containing less or no tungsten than cemented carbides has become an important research topic in the field of wear-resistant hard materials.

![Figure 1. World tungsten mine production.](chart.png)
TiC base cermet was first studied as heat-resistant alloys in the 1950ies. Since then, the addition of Mo$_2$C (Mo) and TiN (N) to the cermet has remarkably improved their mechanical properties and microstructure. Hence, TiC cermet was developed as cutting tool materials. Today, TiC base cermet is the most promising alternative material to cemented carbides [2, 3]. However, difficulties in the large-scale sintering and in the machinability by a diamond wheel hinder many potential applications.

Borides are more stable than nitrides at high temperatures. Duschanek et al [4] summarized the thermodynamic calculation and experimental results on B-C-Ti systems. No ternary compounds exist in this system. Mutual solid solubilities among the binary borides and carbides are very small. Cola et al [5] and Singh et al [6] studied TiC/TiB$_2$-Ni cermet, which showed relatively good mechanical properties after addition of Mo$_2$C and Ni/Mn binders. However, the phase formation and relationship between the mechanical properties and microstructure of the TiC cermet upon addition of boride are still unclear.

Preliminary investigation suggested that TiC/TiB$_2$-19Mo$_2$C-24Ni (mass%) cermet had not only fine microstructure, but also some unknown large grains which might degrade the fracture strength. In this investigation, we studied the effects of Mo$_2$C content (< 19%) on the microstructure and mechanical properties of the TiC/TiB$_2$ base cermet.

2. Experimental procedure
Table 1 shows the specimen compositions used in this investigation. TiC and TiB$_2$ ratio is set to molar ratio of 59:41 which is near quasi-eutectic composition [4].

| Symbol | Composition (mass%)          |
|--------|------------------------------|
| 17Mo$_2$C | TiC/TiB$_2$-17Mo$_2$C-24Ni |
| 15Mo$_2$C | TiC/TiB$_2$-15Mo$_2$C-24Ni |
| 13Mo$_2$C | TiC/TiB$_2$-13Mo$_2$C-24Ni |
| 11Mo$_2$C | TiC/TiB$_2$-11Mo$_2$C-24Ni |

The powder mixtures were ball-milled in acetone to an average particle size of about 1 µm. Raw material powders were TiC (Japan New Metals, particle size 1.5-2.5 µm), TiB$_2$ (Japan New Metals, average particle size 3.38 µm), Mo$_2$C (Japan New Metals, average particle size 1.57 µm) and carbonyl nickel (INCO type 123, average particle size 3.70 µm). The powder mixtures were dried and pressed into green compacts, which were sintered in vacuum for 1 h at 1673 and 1723 K. Mechanical properties were evaluated through the sintered density, transverse rupture strength (TRS) and Rockwell A scale hardness of the sintered compacts. The TRS test was conducted on 4.0 × 8.0 × 25 mm$^3$ test specimens in three-point loading mode with a 20 mm span. X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) were used for microstructural analysis.

3. Results and discussion

3.1. Sintered density
Figure 2 shows the density of the sintered cermet as a function of Mo$_2$C content. The density increases with increasing Mo$_2$C content and is temperature independent.

3.2. Transverse rupture strength
Transverse rupture strength (TRS) of the cermet is shown in figure 3. TRS shows a maximum of 0.83 GPa for the cermet containing 13% Mo$_2$C and sintered at 1673 K, and then decreases with increasing
Mo$_2$C content at both sintering temperatures. The cerments sintered at 1673 K have higher TRS than those sintered at 1723 K for all Mo$_2$C concentrations.

![Figure 2. Density of TiC/TiB$_2$ base cerments sintered at 1673 and 1723K as a function of Mo$_2$C content.]

3.3. Hardness
Figure 4 shows that Rockwell A scale hardness of the cerments has a maximum of 92.6 R$_A$ at 13% Mo$_2$C and then decreases with increasing Mo$_2$C content at both sintering temperatures. The cerments sintered at 1673 K have higher hardness than those sintered at 1723 K for all Mo$_2$C concentrations, same as TRS. The cermet containing 13% Mo$_2$C has better combination of TRS and hardness than other cerments.

![Figure 4. Hardness of TiC/TiB$_2$ base cerments as a function of Mo$_2$C content]

3.4. Phase formation
CuK$\alpha$ XRD analysis was performed to identify the phases formed during sintering of the cerments (see figure 5). All the cerments mainly consist of TiC, TiB$_2$, Mo$_2$C and Ni. Small amounts of unknown phases were also detected in these cerments. No ternary compounds or other kinds of carbides and borides, except for TiC and TiB$_2$, are detected in accordance with Duschanek et al [4].
3.5. Microstructure
Microstructure of the cermets was studied by SEM. Figure 6 shows back scattered electron images of the cermets. Boride-added cermets have finer microstructure than the cermet with no boron shown in figure 7; they still maintain core-rim structure characteristic of TiC base cermets. The coarse white grains are observed in cermets with 15 and 17 Mo$_2$C. The white grains might be Mo-Ni intermetallic compound, as suggested by the electron probe microanalysis (EPMA), and their white color indicates presence of heavy atoms such as molybdenum. Unknown peaks observed in XRD patterns are thought to result from the white phase. Some micro-pores were also observed at the fractured surfaces. Degradation of the mechanical properties of the cermets is attributed to these large white grains and micro-pores. Further enhancement of mechanical properties needs the reduction of micro-pores by the improvement of wettability of the binder phase.

Figure 5. X-ray diffraction results of TiC/TiB$_2$ base cermets Sintered at 1673K

Figure 6. Back scattered electron images of TiC/TiB$_2$ base cermets Sintered at 1673K

Figure 7. Back scattered electron images of TiC-19Mo$_2$C-24Ni cermet.
4. Conclusion
The effects of Mo$_2$C content on the microstructure and mechanical properties of the 59TiC/41TiB$_2$ (molar ratio) base cerments were studied using the model cerments with composition of TiC/TiB$_2$- (11-17)Mo$_2$C-24Ni (mass%).

Both transverse rupture strength and hardness showed maxima for the cermet containing 13% Mo$_2$C. This cermet had fine microstructure without large intermetallic grains, which degrade the mechanical properties.

TiC cermet containing TiB$_2$ achieved remarkable microstructural refinement and still maintained characteristic core-rim structure of the TiC base cerments.

TiC/TiB$_2$ cerments are good alternative material to cemented carbides, in addition to TiCN base cerments.

References
[1]  http://minerals.usgs.gov/minerals/pubs/mcs/2008/mcs2008.pdf
[2]  Lyubimov V D, Élinson D S and Shveikin G P 1992 Soviet Powder Metall. and Met. Ceram., 30 957
[3]  Pastor H 1999 Adv. Sci. Technol. Sinter. Stojanović et al (New York: Kluwer Academic/Plenum Publishers) p 461
[4]  Duschanek H, Rogl P and Lukas H L 1995 J. Phase Equilibria 16 46
[5]  Cola P L, Vallauri D, Maizza G, Amato I and Shcherbakov V A 2001 Int. J. Self-Propag. High-Temp. Synth., 10 451
[6]  Singh M, Rai K N and Upadhyaya G S 2001 Mater. Chem. Phys. 67 226