Mechanical Properties of Boride Cermet at High Temperature

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Cermet is the composite material of ceramics and metal. This material is expected to maintain both the prominent properties of ceramics and metal. At present, only the carbide cermets are put in practical use as the mechanical properties of other cermets are not so good.

New boride cermets,  $Zr_{2}^{2}$ -Fe cermet and MoB-Ni cermet, are developed now. Their mechanical properties at room temperature are equal to Ti-Mo-Ni-C cermet. However, the decrease of strength and hardness of these boride cermets as increasing temperature is extremely small, compared with carbide cermets. Consequently, their mechanical properties are superior to WC-Co hard alloy at elerated temperatures from 600°C to 800°C.

### 1. Introduction

#### 1.1 Cermet

Cermets are ceramic-metal composite materials based on ceramics. Their microstructure consist of ceramic particles and metal layer, and the ceramic particles are bonded by the metal layer. Cermets are expected to have both peculiarities of ceramic (i.e. high hardness and corrosion resistance) and metal (i.e. high-toughness). However it is not easy to satisfy these requirments.

Properties of cermet are affected by the boundarys of ceramic particles and metal layer in addition to the properties of ceramics and metal themselves. To obtain the high boundary strength, it is necessary to satisfy two conditions. The first is the good wettability between the ceramic particle and metal. The second is that any brittle product is not created by the reaction at the boundary. A few combination of ceramics and metal satisfy the both conditions. At present, most of the cermet to be put in practical use are composite materials of metal-carbide and metal. Several carbides can be solve into iron-group-metal at high temperature.<sup>1)</sup> The above conditions are actualized at the boundary of such combinations.

The solvility of wolfram carbide (WC) into cobalt metal (Co) is good at high temperature, and the Young's modulus and hardness of WC are extremely high. Therefore, WC-Co cermet, called as cemented carbide, is put in practical use variously. As several works to improve its properties have been performed in this decade, the uses of cemented carbide extended broadly.

The titanium carbide bonded with nickel cermet (TiC-Ni cermet) shows worthwhile properties comparatively. Moreover, the addition

of molybdenum raises its mechanical properties<sup>2)</sup> and the nitrogen is effective on the improvement of its brittleness.<sup>3)</sup> Therefore, TiC-Ni cermets containning both No and Ni are utilized as tool tips. However, these carbide cermets can not be used in air at high temperature due to the poor oxidation resistance. Other carbide cermets have hardly been used in practice, except for  $Cr_3C_2$ -Ni,Cr cermet which is sometimes utilized as the protection coating against corrosion. A few cermets consisting of metal-oxide or metal-nitride and metal have been studied, but the satisfactory properties have not been obtained.

# 1.2 Boride cermet

It has been well known that many metal-borides have high hardness, high melting point and so on, but the utilization of metal boride has been limited in restricted uses.<sup>4,5)</sup> Recently the zirconium diboride began to use in iron manufacture process.<sup>6)</sup>

Few boride cermets have been developed, because the wettability of metal and boride is not so good in most cace and extremely brittle products are created at the boundary by reaction of boride and metal.<sup>7)</sup> Therefore, we studied about various boride cermets, and concluded that  $ZrB_2$ -Fe cermet and MoB-Ni cermet might be put in practical use.

Figure 1 shows the details of development of these cermets. The reaction products are not observed evidently in the  $ZrB_2$ -Fe cermet, but the wettability of molten Fe on  $ZrB_2$  is not good.<sup>8)</sup> Therefore, the additinal elements, W and WB, are prepared to improve the wettability. While MoB reacts with Ni actively, and a new compound,  $Mo_2NiB_2$ , is obtained. As this compound can solve

into Mi phase partially at high temperature, the wettability of the both is good.

In this paper, we desribe about these boride cermets.

### 2. Process

The process of ZrB<sub>2</sub>-Fe cermet and MoB-Ni cermet is shown in Fig.2. All the materials are supplied as fine powder. Purity and average particle sizes of metal-borides are 99.5% over and 3-7µm, respectively. Mixtures of the boride powder and the metal powder are milled in solvent for 24-72 hours.

The dried powder of ZrB<sub>2</sub>-Fe system is stuffed into the carbon mould, and is sintered in vacuum by hot-press method. While, MoE-Mi powder is compacted by cold isostatic pressing, and is sintered in vacuum without pressure.

The microstructures and phases of the sintered cermets are analysed by X-ray diffraction, SEM-EDAX, TEN. Moreover, their mechanical properties, bending strength, hardness and fracture toughness (K1c value), are determined by various measurements method. 3. Properties of boride cermet

# 3.1 ZrB2-Fe cermet

### 3.1.1 Mechanical properties

At the boundary of  $ZrB_2$  and Fe, chemical compounds are hardly observed. However, the mechanical properties of cermet consisted of only  $ZrB_2$  and Fe are not so good due to the poor wettability.<sup>3)</sup> The wolfram (W) and the tungsten-monoboride (WB) are supplemented into  $ZrE_2$  and Fe to improve the properties. The bending strength is raised about ten per-cent and twenty per-cent, respectively, with the addition of wolfram and tungsten-monoboride.<sup>9)</sup>

The mechanical properties of  $ZrB_2$ -WB-Fe-W cermets are summarized in Fig.3. The contents of W and WB are fixed at 8% of total metal content and 20% of total boride content, respectively. In this Figure 6 is three-point bending strength and Hv is Vickers hardness and K<sub>1</sub>c is fracture toughness determined by Cheveron-notch method. The bending strength increases with increase of metal content, but it is thogth that it is saturated at metal contend about 50%. The K<sub>1</sub>c valure is proportional to the metal contents, and is 13 MN/m<sup>3/2</sup> at 30%. While the hardness decreases with increase of metal content.

### 3.1.2 Microstructure

Figure 3 shows the microstructure of  $ZrB_2-15\%WB-27.5\%Fe-2.5\%W$  cermet. Comparatively round particles are  $ZrB_2$  and their average size is about 5 µm. The dark region, which looks like canal, is corresponds to Fe-alloy. The bright region correspond to the new compound (WFeB) created during sintering. It is thought that the effect of W and WB is caused by the creation of MFeB.

Moreover, the microstructure of this cermet is analyzed with TEM in detail (Fig.5). This analysis shows that wolfram and iron diffuse into  $\text{ZrB}_2$  fairly well. These diffusions is effective to the improvement of wettability of  $\text{ZrB}_2$  and Fe. It is thought that WFeB may solve into iron phase at high temperature,<sup>9)</sup> but the solvility between  $\text{ZrB}_2$  and iron is hardly expected. Therefore, it is thought that these diffusions are due tho the creation of WFeB.

3.2 MoB-Ni cermet

#### 3.2.1 Nechanical properties

The MoB-Ni cermet was studied refer to the result described in 3.1. The compounds obtained from the reaction of VI group metal boride and iron-group metal, are thought to be suitable for element of cermet. Figure 6 is the equilibrium state diagram of Mo-Ni-B ternary phase at  $1000^{\circ}$ C.<sup>11)</sup> We see from this figure that the new metal boride ( $Mo_2NiB_2$ ) is produced from MoB and Ni and this boride can solve into Ni phase. Namely, MoB-Ni cermet is sintered by the reaction to produce  $Mo_2NiB_2$  and the eutectic reaction of  $Mo_2NiB_2$  and Ni. Satisfactory boundary strength and toughness are expected in this cermet.

The effects of metal content on bending strength ( $\sigma$ ), fracture toughness (K<sub>1</sub>c) and hardness (Hv) are shown in Fig.7. The bending strength increases with increase of metal content, and is saturated at about 40%. The K<sub>1</sub>c value is proportional to metal content, but the hardness decreases with increase of metal content. The bending strength, K<sub>1</sub>c value and hardness of the MoB-Ni cermet with 35% metal content are 2.1 GPa, 17.5 MN/m<sup>3/2</sup> and 1050, respectively, and this cermet is a sort of the most tough cermet.

### 3.2.2 Microstructure

The microstructure of MoB-Ni cermet is shown in Fig.8. Main hard particle is  $Mo_2NiB_2$ , but  $W_2NiB_2$  is obserbed too because WB is added to raise hardness of cermet in this case. The hard particles of this cermet are separated more thoroughly compared with  $ZrB_2$ -Fe cermet, their microstructure is similar to the cemented carbide. It is thought that superiority of this cermet on toughness is caused by this separation.

### 3.3 Mechanical properties at high temperature

The relation between bending strength and temperature in ZrB<sub>2</sub>-Fe cermet, MoB-Ni cermet and cemented carbide is shown in Fig.9. Bending strength of cemented carbide decreases rapidly with increase of temperature, but strength of these boride cermet hardly decrease up to 800°C. Moreover, the decrease of Vickers hardness in boride cermet with increase of temperature is relatively small (Fig.10).

It is thought that this predominances of the boride cermet over the cemented carbide is due to the high oxidation resistance of boride, the configuration of hard particle in cermet and sc on. These mechanism must be studied in detail hereafter.

4. Conclusions

Two sorts of boride cermet, which have high strength and toughness, are developed.

The first is ZrB<sub>2</sub>-Fe cermet. This cermet is sintered by hot pressing. The microstructure consists of ZrB<sub>2</sub>, Fe alloy and WFeB, and WFeB plays important roll to improve mechanical properties of this cermet.

The second is MoB-Ni cermet. This cermet is intered by the reaction of MoB and Ni to produce  $Mo_2NiB_2$  and eutectic reaction of  $Mo_2NiB_2$  and Ni.

Mechanical properties at room temperature of these boride cermets are equal to Ti-Mo-Ni-C cermet, but the decrease of strength and hardness of these boride cermets as increasing temperature is extremely small compared with carbide cermets.

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Fig. 2 Process to fabricate the boride cermet.







Fig. 4 Microstructure of ZrB<sub>2</sub>-Fe cermet.



Fig. 5 TEM obserbation of  $ZrB_2$ -Fe cermet.



Fig. 6 Equilibrium state diagram of No-Ni-B phase at 1000°C (after Kolomytev and N.V. Moskaleva).



Fig. 7 Mechanical properties of MoB-Ni cermet at room temperature.











