

Effect of Carbide and Nitride Addition on the Strength of Sintered TiC-Mo₂C-Ni Carbides

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The effect of TaC, VC, Cr₃C₂, NbC, and TiN additives on the strength and hardness of sintered TiC-Mo₂C-Ni hard metals was studied. The additive powder was mixed separately with the TiC-Mo₂C-Ni base powder. The powder mixtures were then compacted and sintered in a vacuum. Experimental results showed that the transverse rupture strength of sintered hard metals was effectively promoted by adding the VC and TiN powders, respectively. However, no additives increased the hardness value of the base materials.

Keywords carbide and nitride additives, sintered TiC-Mo₂C-Ni hard metal, transverse rupture strength

1. Introduction

The sintered hard metals (WC series and TiC series) have been fully developed for several decades and are commercially used as cutting tools, forming dies, and anti-wear parts. Many works have since been devoted to improving the properties of hard metals. For instance, TaC, TiN, and TiC were separately added to the WC-Co alloy to improve the resistance of high-temperature oxidation.^[1] TaC and NbC powders as additives were mixed with WC-Co powder to promote the transverse rupture strength (TRS) and resistance to high-temperature deformation.^[2] Cr₃C₂ powder has been added in past works but has resulted in no improvement on the TRS of WC-Co carbides.^[3] TiC, TaC, and TiN powders were added together to the WC-Co alloy to study the effect of TiN/(TaC-TiC) ratio on the TRS and cutting performance of sintered mixed carbides.^[4]

The hardness of TiC is much higher than that of WC and its specific weight is about one-third of that of WC. The TiC-based cemented carbides have also been widely used as cutting materials. WC, TaC, and NbC were separately mixed with the TiC-Mo₂C-TiN-Ni to investigate the effect of additives on the microstructure and sinterability of the powder mixtures.^[5,6] The addition of small amounts of TaC, NbC, VC, Cr₃C₂, ZrC, HfC, and WC to the TiC-Mo₂C-Ni was conducted to study the effect of additives on the high-temperature strength of sintered base carbides.^[7] In the present investigation, TaC, VC, Cr₃C₂, NbC, and TiN powders were separately mixed with the TiC-Mo₂C-Ni base powder, compacted, and sintered to explore the effect of adding these additives on the hardness and TRS of the sintered mixed carbides.

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2. Experimental

The main components of the matrix material are TiC, Mo₂C, and Ni powders; the additives are TaC, NbC, Cr₃C₂, VC, and TiN powders. Physical characteristics of these powders are listed in Table 1. For the group of powder mixtures containing additives such as TaC, NbC, Cr₃C₂, and VC, the Ni content was 10 wt.%, and for the other group containing TiN, the Ni content was 13 wt.%. The ratio of Mo₂C/TiC was kept 1:4. The powder mixture was ball-milled in an alumina ball mill for 24 h. The ball-milled powder mixture was then dried, granulated, compacted with a pressure of 149 MPa, dewaxed, and sintered in vacuum (10⁻⁴ torr.) at 1400 °C, 1460 °C, and 1520 °C for 40 min. The linear shrinkage after sintering was about 20%. The sintered specimens were ground to meet the dimension requirement for the transverse rupture strength (TRS) measurement (40 mm × 8 mm × 8 mm). The bending test (powder supplier; H.C. Starck, Berlin, Germany) was conducted to measure the TRS of sintered carbides at room temperature. The Rockwell hardness tester was used to obtain the HRA hardness values.

3. Experimental Results

3.1 Effect of Additive Content on the TRS of Sintered Mixed Carbides

Figure 1 shows the relation between the added amount of TaC, NbC, Cr₃C₂, and VC, and the TRS of mixed carbides sintered at 1460 °C for 40 min. The TRS of TiC-Mo₂C-Ni carbide always decreased with addition of Cr₃C₂. Separately added TaC, VC, or NbC powders strengthened the base carbide. The VC powder appeared to be the most effective strengthening additive; adding 1 wt.% of this powder resulted in a 20% increase in TRS. How the TiN content and the sintering temperature affected the TRS of the sintered matrix carbide is depicted as Fig. 2. The TRS of the sintered matrix material without the additive increased with the increasing sintering temperature. However, as the sintering temperature was raised to 1520 °C, the TRS inversely decreased. The TRS of the sintered mixed carbides increased with increasing TiN content,

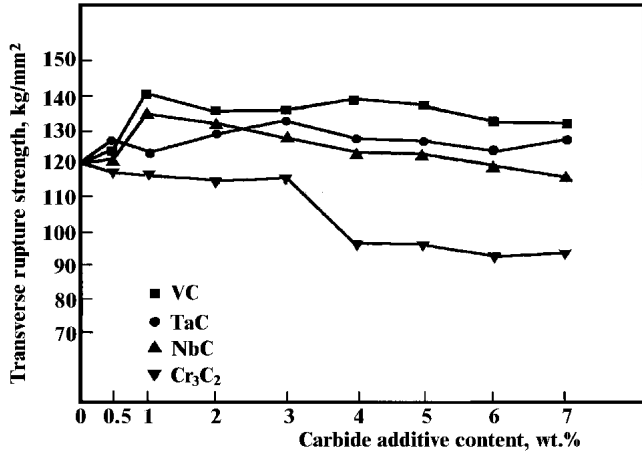


Fig. 1 Variation of the TRS of sintered carbides with the carbide additive content

Table 1 Physical Characteristics of Carbides and Nitride

Powder	Crystal Structure	Average Particle Size, μm	Microhardness, kg/mm^2
TiC	BCC	1.4	2900
VC	BCC	3.2	2900
NbC	BCC	1.5	2400
TaC	BCC	1.1	2500
Cr ₃ C ₂	Ortho	5.7	1300
Mo ₂ C	Ortho	4.2	1500
TiN	BCC	1.5	2000

reached a maximum at 15 wt.%, and then decreased. The optimum sintering temperature was 1460 °C.

3.2 Effect of Additive Content on the Hardness of Sintered Mixed Carbides

The variation of hardness values of sintered base carbides with the content of TaC, VC, NbC, and Cr₃C₂ is shown in Fig. 3. All the carbide additives decrease the hardness value of sintered base carbides. The hardness values dropped as the additive was being introduced. However, the hardness decrement resulted from adding the carbide additives, which are always within 1 HRA. Figure 4 reveals that the addition of TiN also decreases the hardness of sintered mixed carbides. The hardness dropping increases with increasing TiN content and sintering temperature.

4. Discussion

The results of the TRS measurement show that the TiC-Mo₂C-Ni matrix is strengthened by adding the TaC, VC, and NbC carbides. With the same face centered cubic (fcc) crystal structure, the TaC, VC, and NbC carbides are ready to form a solid solution with the TiC carbide during sintering that results in a strengthening effect.^[7,8] The Cr₃C₂ carbide possesses a crystal structure (orthogonal) different from that of TiC (FCC); solution strengthening induced by this additive is negligible.

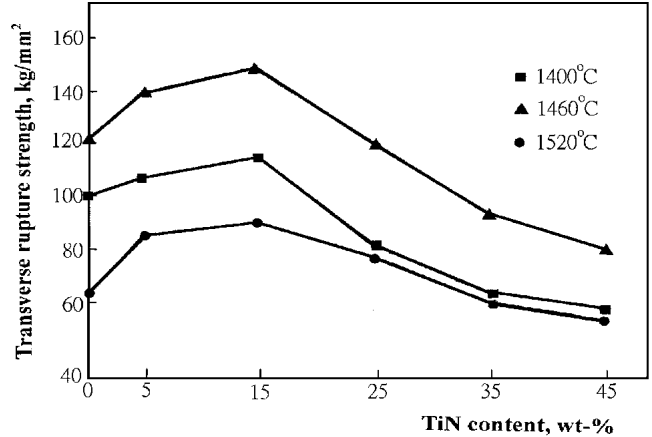


Fig. 2 Variation of the TRS of sintered carbides with the TiN content and the sintering temperature

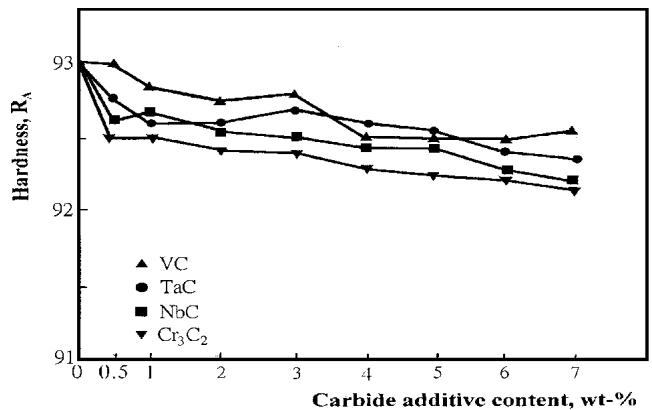


Fig. 3 Variation of the hardness of sintered carbides with the carbide additive content

Figure 3 reveals that introducing any kind of carbide additive decreased the hardness of sintered mixed carbides. Referring to Table 1, it can be seen that the hardness of most carbide additives was lower than that of the TiC carbide. Therefore, the more additives, the softer the sintered mixed carbides. The Cr₃C₂ carbide is the softest one among these additives; therefore, it results in a pronounced softening effect.

The way that the TRS of sintered mixed carbides varies with the TiN content is shown in Fig. 2. The optimum added amount of TiN is about 15 wt.%. The TiN reacts with TiC to form Ti(C, N) during sintering.^[9,10] The hardness of Ti(C, N) is lower than that of TiC; therefore, the hardness of sintered mixed carbides decreases with increasing TiN content. However, the toughness of Ti(C, N) was better than that of TiC, and formation of Ti(C, N) inhibited the growth of TiC particles during the liquid-phase sintering.^[11] Therefore, the TRS of sintered mixed carbides increases with increasing TiN content.

Upon vacuum sintering, denitriding of TiN occurs. The TiN partially decomposes to form TiN_x (where $x < 1$), and N₂ gas generates from the combining of nitrogen atoms.^[12] In the case of TiN content being less than 15 wt.%, denitriding is not serious. The toughness enhancing and grain growth inhib-

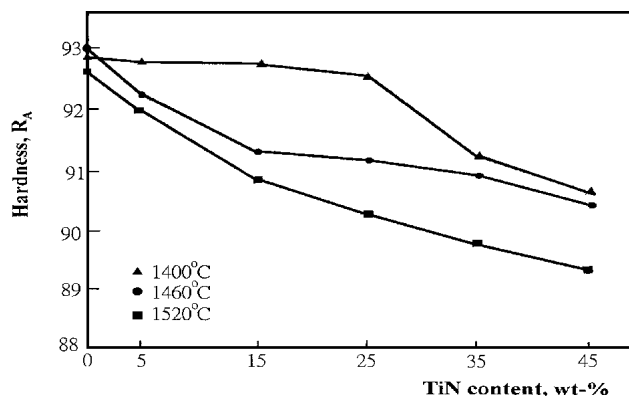


Fig. 4 Variation of the hardness of sintered carbides with the TiN content and the sintering temperature

iting mechanisms are dominant and lead to strengthening of TiN-added TiC-Mo₂C-Ni carbides. When the TiN content is further increased, the N₂ gas increases greatly in volume and induces many micro-pores that will subsequently weaken the sintered mixed carbides. At the same time, the wettability of TiN with the Ni-based binder phase is poor, and the more the TiN content, the worse the densification. Therefore, the TRS of sintered mixed carbide decreases with increasing TiN content, as the TiN is added more than 15 wt.%.

The volume of Ti(C, N) solid solution increased with increasing sintering temperature. Therefore, the TRS of carbides sintered at 1460 °C is higher than that sintered at 1400 °C. However, since the Ti(C, N) is softer than TiC, variation of hardness values with the sintering temperature exhibit a reverse tendency. As the sintering temperature is further increased, the N₂ gas generated from decomposition of TiN also greatly increases in volume, which results in internal pores letting the TRS and hardness of carbides sintered at 1520 °C become lower than both sintered at 1400 °C and 1460 °C.

5. Conclusions

The following conclusions can be drawn from this work. First, the addition of TaC, VC, or NbC carbides promotes the room temperature TRS of the TiC-Mo₂C-Ni hard metal.

Strengthening behavior of the TiC-Mo₂C-Ni hard metal obtained by adding these additives is similar, but the VC carbide exhibits a better promoting effect. The addition of carbide additive slightly decreases the hardness value of the TiC-Mo₂C-Ni hard metals. Second, the addition of TiN nitride can also strengthen the TiC-Mo₂C-Ni hard metal through formation of the Ti(C, N) solid solution and the particle growth-inhibiting mechanism. The select content of TiN nitride is about 15 wt.%, and the recommended sintering temperature is 1460 °C. The addition of the nitride additive always decreases the hardness of the matrix materials.

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