Study on Strengthening of Graphene and Carbon Nanotube to Shield Machine Carbide Cutter

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Abstract. It has been found that thermal effects play a major role in the failure of cemented carbide tools. In order to improve the service life of carbide cutting tools, the high temperature strength and thermal conductivity of the cutting tools should be further improved. Graphene has the highest thermal conductivity and high temperature hardness, and carbon nanotubes (CNTs) have high strength and toughness. The graphene and CNTs strengthen Co phase with dispersion strengthening and fiber strengthening mechanism by dispersing uniformly to WC-Co cemented carbide with an appropriate ratio and clustering around WC particles, furthermore, it could reduce its operating temperature by drastically increasing the thermal conductivity.

Introduction

At present, the construction of China's subways, high-speed railways and highways is being fully carried out and the use of large shield machines is increased [1, 2]. Reducing the consumption of cutting tools is the main mean to reduce tunneling costs and improve working efficiency [3-5]. The engineering practice in recent years has found that when excavating in the soft and hard uneven strata, the tool life is sometimes even lower than excavating in the simple hard rock. To explore the causes, we found that when the shield machine worked in the uneven strata, the tool would be affected by higher temperature, and the severe eccentric wear would occur. Therefore, we can solve the problem by improving the thermal conductivity and thermal strength of the tool materials.

Following this new idea, this project put forward the aim of adding graphene and CNTs to the low cobalt coarse grained cemented carbide with suitable proportions, exerting their respective characteristics and toughening cemented carbide in order to improve the properties of the present tool material [6-10].

Experimental Materials and Method

The specimens used in the experiment were made by SPS sintering. The process of preparing specimens was as follows:

First, a certain mass proportion of WC powder(94wt%) and Co powder(6wt%) are poured into a ball milling can, adding graphene and carbon nanotube powder shown in Table 1, respectively. Then, add certain amount of ethanol solution to make the powder completely wet.

Put the milling ball into the milling can, cover the lid, tighten the screws and take the air out of the ball milling can with air pump. Mix WC, Co, graphene and carbon nanotubes for 4 hours under 100rpm ball milling speed. After ball milling, open the lid and dry the mixture in the vacuum dryer.
<table>
<thead>
<tr>
<th>Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<th>11</th>
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<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene (wt% compared with Co)</td>
<td>0</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>1.5</td>
</tr>
<tr>
<td>Carbon nanotubes Content (wt%)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.2</td>
<td>0.4</td>
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</tbody>
</table>

Synthesizing the previous research results, the sintering temperature of SPS was set at 1200°C. The heating rate was 100/min and the pre pressure was 25MP. When the temperature raised to 1200°C, the pressure increased to 80MP, for 10min. The sintering mold is high strength graphite mold with an inner diameter of 15mm.

During the experiment, the mixed powder was poured into a high strength graphite mold with graphite paper around the inner surface. Then put the mold in place as shown in Figure 1, close the lid, and drained out the air with the vacuum valve closed. Pre-added a certain amount of pressure, and adjust the infrared thermometer to temperature measurement hole of the mold. When the vacuum degree reached the predetermined value, activate the infrared temperature measuring mode and start sintering process with sintering power on and the required sintering program started.

When sintering ended, cooled the sample in the furnace, closed the sintering program and entered the temperature measurement mode. When the temperature reduced to 600°C, adjust to the thermocouple temperature measurement mode, and then opened the vacuum valve to deflate when reduced to 200°C. When the internal and external pressure was consistent, opened the lid and continued to cool down to lower temperature. Then took out the graphite block and the mold, remove the sample and scrape off the graphite paper on the surface. Got the sample as shown in Figure 2.

This tested sample was cemented carbide, so the A scale was used, and the test force is 588.4N (60kgf). After fine grinding, the sample was tested on HR-150A type Rockwell hardness tester, and each sample was randomly taken eight points, and the average value was taken as the final value of hardness of the sample.

The sample with a diameter of 15mm was grinded to the thickness of 1.5~3mm, and the graphite sticking on the surface from the SPS sintering process was removed. Then, the thermal diffusivity was measured at 500°C. Three points of each sample was tested and took the average. The specific heat of the sample was calculated by the specific heat and mass fraction of each component.

The formula for calculating heat conductivity is:

\[
\lambda = \alpha \times C_p \times \rho
\]  

(1)

In this formular,

\(\lambda\) — thermal conductivity (w/(m·K));
\[ \alpha \text{—thermal diffusivity (cm}^2/\text{s}); \]
\[ Cp \text{—specific heat (J/(g·K));} \]
\[ \rho \text{—density (g/cm}^3). \]

Results

Content Effect of Graphene on Hardness of WC-Co Cemented Carbide

As shown in Table 2, not too much influence on the hardness increase of graphene, there might be three reasons: 1. the adding amount was too little; 2. the dispersion did not reach an ideal state; 3. there is no hardness enhancement mechanism of graphene. Specific reasons would be further explored in the subsequent experiments.

Table 2. Hardness of WC-Co cemented carbide with different content of graphene.

<table>
<thead>
<tr>
<th>Graphene content (wt% compared with Co)</th>
<th>HRA initial data</th>
<th>HRA</th>
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</thead>
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<tr>
<td></td>
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<tr>
<td>0</td>
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<tr>
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<td>89.5</td>
<td>89.5</td>
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</table>

Content Effect of Carbon Nanotube on Hardness of WC-Co Cemented Carbide

As shown in Figure 3, with the addition of carbon nanotubes of 0.1wt%, 0.2wt%, 0.3wt%, 0.4wt%, 0.5wt% and 0.6wt%, the hardness of the alloy increased first and then decreased. The reason might be that with the excessive addition of carbon nanotubes, the cluster phenomenon occurred and the grain size would be uneven, which caused the decrease of hardness.

Figure 3. Effect of carbon nanotube content on hardness.

Content Effect of Graphene on Thermal Conductivity of WC-Co Cemented Carbide

As shown in Table 3, the thermal diffusivity increased obviously after adding graphene, and the specific heat increased slightly, and the density decreased slightly. The thermal conductivity was calculated by synthesizing the preceding parameters, as shown in Table 3, we found that the thermal conductivity increased greatly after adding graphene.

Table 3. Thermal conductivity of WC-Co cemented carbide with different graphene content

<table>
<thead>
<tr>
<th>Graphene content (wt% compared with Co)</th>
<th>Thermal diffusivity [cm²/s]</th>
<th>Specific heat capacity [J/(g·K)]</th>
<th>Density [g/cm³]</th>
<th>Thermal conductivity [w/(m·K)]</th>
</tr>
</thead>
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<td>0.2602</td>
<td>14.24</td>
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<tr>
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<tr>
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<tr>
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<td>0.2623</td>
<td>14.00</td>
<td>64.1570</td>
</tr>
</tbody>
</table>
Conclusion

In order to study the influence of graphene and carbon nanotubes on strength and thermal conductivity of WC-Co hard alloy, the experiment research on the effective dispersion method in WC, Co powder, different proportions of graphene and carbon nanotubes and a certain proportion of WC and Co powder was mixed using ultrasonic and ball milling, and then sintered into cylindrical specimens with diameter of 15mm using SPS sintering technology. The properties were analyzed, the conclusions are as follows:

1. The coarse grained WC-Co cemented carbide samples were successfully sintered by means of SPS, the relative density reached 99.37%, and Rockwell hardness (HRA) reached more than 89, which exceeded the requirements of the same proportion of Co content mining tools.

2. The hardness of alloy decreased slightly when adding 1% and 1.5% content of graphene with Co, but the hardness increased slightly when adding to 2%. However, compared with the sample without addition, the hardness increased 0.56%, the effect was not significant.

3. The thermal conductivity of alloy decreased slightly when adding 1% content of reductive graphene with Co, but the thermal conductivity significantly increased when adding to 2.5%. Compared with the sample without addition, the thermal conductivity increased 8%.

References