Original Article

Effects of Cr concentration on the microstructure and properties of WC-Ni cemented carbides

Guoping Li, Yingbiao Peng, Lianwu Yan, Tao Xu, Jianzhan Long, Fenghua Luo

State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan, 410083, PR China
College of Metallurgical and Materials Engineering, Hunan University of Technology, Zhuzhou, Hunan, 412008, PR China
State Key Laboratory of Cemented Carbide, Zhuzhou, Hunan 412000, PR China

ABSTRACT

Based on thermodynamic calculations, WC-Ni-Cr3C2 model alloys with high Ni content have been designed by fixing the carbon potential to form either graphite or eta (M6C) phases. The solubility of the grain growth inhibitor Cr3C2 in the Ni binder phase has been experimentally determined by electron-probe microanalysis and compared with thermodynamic calculations. Five alloys with different Cr3C2 contents were prepared considering the observed solubility limit and compared with a Cr-free alloy. The effects of Cr3C2 addition on the microstructures, corrosion resistance, and mechanical properties of WC-Ni cemented carbides were studied using optical microscopy (OM), scanning electron microscopy, chemical examinations, and mechanical property tests. Our results indicate that an increase in the Cr3C2 concentration results in a decrease in both the density and the fracture toughness of cemented carbide samples. The maximum hardness was obtained with the addition of 0.75 wt.% Cr3C2. The corrosion resistance of WC-Ni cemented carbides in H2SO4 solution can be significantly improved with the addition of Cr3C2.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Cemented carbides consist of numerous refractory carbides embedded within a ductile binder phase. These carbide materials are widely used in many industrial applications including cutting tools, geo-engineering equipment, and wear-resistant parts. These applications are largely due to their unique and excellent properties like high hardness, high Young's modulus, high strength, and high resistance to wear [1-4]. Tungsten carbide-nickel (WC-Ni) cemented carbides show better oxidation and corrosion resistance compared with tra-
ditional tungsten carbide-cobalt (WC-Co) cemented carbides [5,6]. However, the hardness and the strength of the WC-Ni are lower than those of the WC-Co cemented carbides [7,8]. Recently, the substitution of cobalt with nickel, in whole or part, has been investigated to strengthen the binder phase, as well as reduce the costs associated with the limited supply and the high market price of cobalt powder [9-11]. Various carbides such as VC, Cr$_3$C$_2$, Mo$_2$C, TaC, TiC, and ZrC, have been added to WC-Ni-based cemented carbides to enhance their properties. Correa et al. [12] found that the WC-10 wt.% (Ni-Si) cemented carbide presented a superior flexure strength, a high fracture toughness, and a bulk hardness similar to those of conventional WC-Co cemented carbides. Tsuchiya et al. [13] reported that the transverse-rupture strength and the hardness of the WC-15Ni-Cr$_2$C$_2$ (wt.%), cemented carbide increased with an increased concentration of Cr$_2$C$_2$ (up to 2–3 wt.%). Bernhard et al. [14] found that VC is a highly effective grain growth inhibitor in WC-10Ni (wt.%), followed by TaC, Cr$_3$C$_2$, TiC, and ZrC. Their report indicates that hardness increased with the amount of additive, then plateaued [14]. Shi et al. [15] investigated WC-9Ni (wt.%), cemented carbides for various Cr addition mechanisms, each exhibiting a different immersion corrosion resistance in neutral tap water.

To avoid precipitates which may be deleterious to the mechanical properties, the amount of grain growth inhibitor added to a cemented carbide should not exceed the maximum solubility in the binder phase [16-18]. Recently, Peng et al. [17] and Lauter et al. [18] have investigated the equilibrium solubilities of various grain growth inhibitors in the binder phase of WC-Co cemented carbides through both experimental and computational methods. However, studies have not focused on the effects of Cr$_3$C$_2$ on WC-Ni cemented carbides. Herein, The present work aims to 1) design and prepare WC-Ni-Cr$_3$C$_2$ model alloys with high Ni content, 2) experimentally determine the equilibrium solid-state solubility of Cr in the Ni binder phase at 1100 °C of the WC-Ni-Cr$_3$C$_2$ cemented carbides compared with thermodynamic calculations, and 3) study the microstructures, mechanical properties and electrochemical behaviors of WC-9Ni-Cr$_3$C$_2$ (wt.%) cemented carbides with the addition of grain growth inhibitor Cr$_3$C$_2$ below its maximum solubility in Ni binder phase.

2. Methods

2.1. WC-Ni-Cr$_3$C$_2$ model alloys

To accurately determine the solubility limits of Cr in the Ni binder phase, WC-Ni-Cr$_3$C$_2$ model alloys with a large amount of Ni binder phase were designed to include freely doped carbide, as well as graphite or $\eta$-phases. Thermodynamic calculations aided the design of these alloys based on our established thermodynamic database for cemented carbides [19]. The general methodological details are provided in the work [17].

The compositions of the WC-Ni-Cr$_3$C$_2$ model alloys are listed in Table 1. Samples were prepared following the powder metallurgical route. The composition of the binder phase was measured by electron-probe microanalysis (EPMA).

### Table 1 – Composition of WC-Ni-Cr$_3$C$_2$ model alloys (+C: with free graphite, +eta: with $\eta$-phases).

<table>
<thead>
<tr>
<th>C activity</th>
<th>Composition, wt.%</th>
<th>Predicted equilibrium state at 1100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>+C</td>
<td>Cr</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>+eta</td>
<td>Cr</td>
</tr>
</tbody>
</table>

| +C         | Cr     | W | Ni | WC+C + fcc-Ni + M$_2$C$_3$ + graphite |
|           | +eta   | Cr | W | Ni | WC+C + fcc-Ni + M$_2$C$_3$ + M$_6$C |

### Table 2 – Composition of cemented carbides (wt.%).

<table>
<thead>
<tr>
<th>Cemented carbides</th>
<th>Cr$_3$C$_2$</th>
<th>Ni</th>
<th>WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>9</td>
<td>Balance</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>9</td>
<td>Balance</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>9</td>
<td>Balance</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>9</td>
<td>Balance</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>9</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2. WC-Ni-Cr$_3$C$_2$ cemented carbides

Five WC-9Ni-xCr$_3$C$_2$ (wt.%) cemented carbides doping different amounts of Cr$_3$C$_2$ ($x=0, 0.4, 0.6, 0.75, 0.9$) were prepared according to the compositions listed in Table 2. Powder mixtures were obtained by rolling ball milling for 30 h and in alcohol. The ball-to-powder weight ratio was 10:1. Afterward, the pulp was dried in a thermostatic drying oven at 80 °C for 60 min and 2.0 wt.% paraffin was added as a pressing aid. The mixed powders were granulated through a 100 mesh screen and then pressed into rectangular compacts of 6.5 mm × 5.25 mm × 20 mm. All green compacts were then placed on graphite trays, followed by dewaxing and sintering in an industrial-scale dewaxing low-pressure vacuum sintering furnace at 1450 °C for 60 min. The pressure of the argon atmosphere was set to 55 bar at the final sintering temperature to avoid the prominent evaporation of Ni during liquid-phase sintering. After sintering, the cemented carbides were cooled to room temperature in the dewaxing low-pressure vacuum sintering furnace.

The microstructure characterization of the cemented carbides was carried out by a Quanta FEG250 scanning electron microscope. The densities of the cemented carbides were measured via the Archimedes method. A Buehler Micromet 5100 hardness tester was used to measure the hardness under a load of 30 kg for a holding time of 15 s. The fracture toughness ($K_{IC}$) was calculated from the Vicker’s hardness from the following equation [20]:

$$K_{IC} = 0.15 \cdot (HV_{30}) \left( \frac{1}{L} \right)^{1/2}$$

where $HV_{30}$ is the Vickers hardness, and $L$ (mm) is the micro crack length of the indentation measured by an OM after polishing. Five separated tests under the same conditions
were conducted. Additionally, the corrosion resistance of each WC-Ni cemented carbides was investigated by a CHI 660E electrochemical workstation. The specimens were then connected to an insulated copper wire and coated with an epoxy resin adhesive. The epoxy was abraded at the test surface to expose the cemented carbides surface before the specimens were mounted in resin, providing a thin film around the edges of the test surface which prevents crevice effects [21]. The testing faces were then ground and polished. Electrochemical tests were conducted in a 1 N H₂SO₄ solution at 15 °C using a standard three-electrode system: a saturated calomel electrode (SCE) used as the reference electrode, a platinum sheet used as the counter electrode and the working electrode. Each electrode was connected to the test specimens. The electrochemical conditions were controlled to be a scanning speed of 5 mV/s, an initial potential of 0.5 V, and a final potential of 1.5 V. The polarization curve was obtained by use of the CHI 660E software to analyze and compare the corrosion potential (Ecorr) and the corrosion current (Icorr) under various electrochemical parameters.

3. Results and discussion

3.1. Saturate solid-state solubility

Fig. 1 (a) and (b) present the microstructure of the WC-Ni-C₃C₂ model alloys without the presence of free graphite and free MnC (η), respectively. As can be seen from Fig. 1, the equilibrium phases in the model alloys are consistent with those in the designed phases. The observed saturated solubilities specify the upper and lower solubility limits of various elements in the binder phase of industrially fabricated cemented carbides. Table 3 shows the experimentally determined composition of the binder phase found in the WC-Ni-C₃C₂ model alloys; these results were also compared with the thermodynamic calculations based on our established database [19]. Fig. 2 presents the calculated composition and calculated Ni content of the binder phase with respect to the carbon content for the WC-9Ni-2Cr (wt.%) cemented carbide; the present experimental results are also plotted for comparison. As can be seen, the calculated results agree well with the experimental ones. To further study the effects of Cr₃C₂ on both the microstructures and the properties of WC-9Ni (wt.%) cemented carbide, we limited the addition of the grain growth inhibitor, Cr₃C₂, be less than its maximum solubility in the Ni binder phase in accordance with our present results.

3.2. Microstructure

Fig. 3 shows the microstructure of the WC-9Ni-xCr₃C₂ (wt.%) cemented carbides with various Cr₃C₂ concentrations: (a) 0,
b) 0.4, (c) 0.6, (d) 0.75, and (e) 0.9. As can be seen in Fig. 3(a), WC-9Ni displays an abnormal grain growth of the WC. Overall, the grain size of the WC gradually decreases with an increase in the doping concentration of Cr$_3$C$_2$ (Fig. 3(b)–(e)). Cr$_3$C$_2$ has been widely used as a grain growth inhibitor in ultrafine WC-Co cemented carbides, forming a metastable phase (W,Cr)C at the WC-binder interface [6]. It is very likely that the doping of Cr$_3$C$_2$ in the WC-Ni cemented carbide may likely have similar inhibitory effects on the grain growth in WC.

3.3. Mechanical properties

In Figs. 4 and 5, we provide the density, hardness and fracture toughness of various WC-9Ni-xCr$_3$C$_2$ (x=0, 0.4, 0.6, 0.75, and 0.9) cemented carbide grades. With the increase in Cr$_3$C$_2$ doping from 0 to 0.95 wt.%, the density and fracture toughness decrease significantly. The Vicker's hardness increased with the Cr$_3$C$_2$ content up to 0.75 wt%; however, when the Cr$_3$C$_2$ content exceeded 0.75 wt%, the data show a distinct downward trend. The wettability of nickel towards WC is relatively
poor compared to WC and cobalt [22,23], resulting in a significant decrease in density with the Cr$_3$C$_2$ doping due to an increased interfacial surface between the binder and WC. As can be seen in Fig. 3, many pores exist in the samples and are likely responsible for the decrease in the fracture toughness, see Fig. 5. According to the Hall-Petch relation, the hardness is enhanced due to a refinement of the WC grains. However, the influence of the porosity on the hardness outstrips the effects associated with the refinement of the WC grains when the doping Cr$_3$C$_2$ reaches 0.9 wt%.

3.4. Electrochemical behavior

Potentiodynamic polarization curves of WC-Ni cemented carbides with various degrees of Cr$_3$C$_2$ doping were obtained to probe the influence of Cr$_3$C$_2$ content on the corrosion resistance (Fig. 6). Notable from the potentiodynamic polarization curves, the corrosion potential shifts to more positive values as the concentration of Cr$_3$C$_2$ is increased. Sample 5 (WC-9Ni-0.9Cr$_3$C$_2$) displays the highest corrosion potential, 0.049 V, and the lowest corrosion current density, $6.364 \times 10^{-6}$ A; this indicates that Cr$_3$C$_2$ doping can significantly improve the corrosion resistance of cemented carbides. The corrosion parameters are given in Table 4. The current density of cemented carbide generally decreases after reaching critical current, yet is still higher than typical passivation current density, which is called pseudopassive behavior [24,25]. As can be seen in Fig. 6, WC-Ni cemented carbides exhibit a characteristic anodic behavior, seeing the presentation of pseudopassive regions in the acidic solution.

4. Conclusion

Herein, we have experimentally determined the maximum solubility of the Cr$_3$C$_2$ grain growth inhibitor in the Ni binder phase and compared with thermodynamic calculations based on our established thermodynamic database, which are key information during the development of ultrafine cemented carbides with Ni as the binder phase. At concentrations below its solubility limit in the Ni binder, the addition of Cr$_3$C$_2$ affects the microstructure, physical properties, and corrosion resistance of WC-Ni cemented carbides, which have been systematically investigated within this study. Our results show that Cr$_3$C$_2$ can refine the WC grains; furthermore, an increase in the Cr$_3$C$_2$ concentration results in a decrease in both the density and the fracture toughness. The hardness reaches a maximum with a Cr$_3$C$_2$ doping concentration of 0.75 wt%. Additionally, we show that by increasing the Cr$_3$C$_2$ content, the corrosion resistance of cemented carbides can be significantly improved.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The financial support from the National Natural Science Foundation of China (Grant no. 51601061), Key Research and Development Program of Hunan Province (grant no.
Table 4 – Electrochemical corrosion parameters of the cemented carbides in a 1 N H₂SO₄ solution.

<table>
<thead>
<tr>
<th>Cemented carbides</th>
<th>Ecorr(V)</th>
<th>lcorr(A)</th>
<th>ip(A)</th>
<th>icorr(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.138</td>
<td>2.625 × 10⁻³</td>
<td>9.120 × 10⁻⁵</td>
<td>1.791 × 10⁻⁵</td>
</tr>
<tr>
<td>2</td>
<td>-0.089</td>
<td>6.124 × 10⁻⁴</td>
<td>6.516 × 10⁻⁵</td>
<td>8.640 × 10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td>-0.062</td>
<td>2.512 × 10⁻⁴</td>
<td>2.818 × 10⁻⁵</td>
<td>8.416 × 10⁻⁶</td>
</tr>
<tr>
<td>4</td>
<td>-0.061</td>
<td>1.374 × 10⁻⁴</td>
<td>3.162 × 10⁻⁵</td>
<td>8.208 × 10⁻⁶</td>
</tr>
<tr>
<td>5</td>
<td>-0.049</td>
<td>1.324 × 10⁻⁴</td>
<td>1.995 × 10⁻⁵</td>
<td>6.364 × 10⁻⁶</td>
</tr>
</tbody>
</table>

REMARKS

2019GK2052) and Special Fund for Changzhutan National Independent Innovation Demonstration Zone (grant no. 2018XK2203) is acknowledged. We would like to thank Editage (www.editage.cn) for English language editing.

REFERENCES