Toughening of WC-Co Cemented Carbides by \textit{In-situ} Transformed Carbon Fiber

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Abstract. WC-2Co cemented carbides toughened by in situ transformed carbon fibers were prepared by hot-press sintering at 1450°C using pre-oxidized polyacrylonitrile fibers (PAN$_f$) as the precursor. The phase composition, microstructure and mechanical properties of the samples with different added fractions of PAN$_f$ were investigated. The results show that the PAN$_f$ transformed in situ into carbon fibers at 1450°C during the hot-press sintering. The formed carbon fiber could supply carbon to the sintering system, suppressing the formation of $\eta$ phase and improving the relative density of the samples. With the increase in the added fraction of PAN$_f$, the Vickers hardness of the samples initially increased and then slightly decreased, reaching its maximum of about 1900 HV$_{10}$ with 0.5 wt.% PAN$_f$. The flexural strength and fracture toughness of the samples gradually increased from 530 MPa and 5.5 MPa·m$^{1/2}$ to 700 MPa and 7.5 MPa·m$^{1/2}$ with the increase in the added fraction of PAN$_f$ from 0 to 2 wt.%. The toughening mechanisms were cracks deflection, fiber pull-out and crack bridging.

1. Introduction

Cemented carbides, normally the aggregates of WC particles bonded with metallic binder, are widely employed in metal cutting, wood machining, rock drilling, tunneling, trenching and so on, because of their unique combination of high hardness and good fractural strength [1,2]. However, the presence of metallic binder limits the performance of cemented carbides in applications demanding good high-temperature properties despite it can improve the fracture strength and toughness of cemented carbides. Moreover, the metallic binder is more likely to be attacked than hard phases in corrosion/oxidation environment, which reduced the service life of the components [3,4]. Therefore, many researches are focused on the fabrication of cemented carbides with little amount of metallic binder or even without binder in recent decades [5-9].

However, cemented carbides with little amount of metallic binder phase possess significantly inferior fracture toughness as compared with the conventionally cemented carbides. So the recent interest is focused on toughening such materials. As is reported, nanoparticles, fibers, whiskers, carbon nano-tubes or even unoxidized graphene have been considered to toughen ceramic composites [10-16], in which carbon fiber would be a potential additive for toughening cemented carbides due to its high toughness, high specific strength and good thermal stability [17,18]. Always in literature, carbon fiber was mixed with ceramic powder, suffering long time ball milling before sintering. However, the mechanical properties of carbon fibers can be degenerated during long time ball milling and the high...
cost of carbon fibers increase the cost of production. To overcome such drawbacks, precursors capable of producing carbon fibers are normally applied, in which polyacrylonitrile is considered as the most suitable precursors for producing high-performance carbon fibers (compared to pitch, rayon, etc.) [19]. More recently, attempts have been made to use pre-oxidized polyacrylonitrile fiber (PANf) as precursor to in situ produce carbon fibers to toughen Al2O3 ceramics, and the fracture toughness of the Al2O3 ceramics increased from 4.75 to 6.29 MPa·m1/2 with 20 vol.% PANf addition [17]. And our previous work revealed that after 15 vol.% PANf was added into TiCN-based ceramics, the flexural strength of the cermets increased from 830 to 1020 MPa and the fracture toughness increased from 7.02 to 9.94 MPa·m1/2 [20]. So, here we wonder whether the cemented carbides with little amount of binder can be toughened by in situ transformed carbon fibers from PANf.

In this work, cemented carbides with only 2 wt.% metallic binder Co were prepared by hot-press sintering and the reinforcement of in situ transformed carbon fiber from PANf on them were investigated. As expected, the designed cemented carbides can be significantly toughened by in situ transformed carbon fibers from PANf.

2. Experimental procedure

2.1. Sample preparation

Commercially purchased WC (with a particle size of ~0.6μm, purity of higher than 99.5 % and density of 15.63 g/cm3), Co (with a particle size of ~1.5 μm, purity of higher than 99.9 % and density of 8.79 g/cm3) and VC (with a particle size of ~4 μm, purity of higher than 99.0 % and density of 5.78 g/cm3) powders were used as initial raw materials in this work. A pre-oxidized PANf (pre-oxidized at 300°C, ~2 mm long, and with a density of 1.4 g/cm3) was used as the precursor for in situ producing carbon fiber. The designed compositions of the samples are listed in Table 1.

| Powders | WC (wt.%) | Co (wt.%) | VC (wt.%) | PANf (wt.%) | PANf (vol.%) |
|---------|-----------|-----------|-----------|-------------|-------------|
| WCVP-0  | 97        | 2         | 1         | 0           | 0           |
| WCVP-0.5| 96.5      | 2         | 1         | 0.5         | 5.16        |
| WCVP-1.0| 96        | 2         | 1         | 1.0         | 9.87        |
| WCVP-1.5| 95.5      | 2         | 1         | 1.5         | 14.16       |
| WCVP-2.0| 95        | 2         | 1         | 2           | 18.11       |

During processing the samples, the ball-milling included two stages. In the first stage, WC, Co and VC were mixed according to the designed compositions and ball milled for 48 h in a high-energy attrition mill (Model: SY-1, China) in alcohol with Φ5 mm YG-6 cemented carbides balls (ISO: K20) as milling media. The ball-to-powder mass ratio was 10:1 and the rotational speed was 300 rpm. In the second stage, PANf, which had been dispersed for 15 min by ultrasonic vibration in alcohol, were added into the mixed powder slurry. Then the mixed slurry continued to be ball milled for 2 h with a rotational speed of 100 rpm. After milling, the slurries were dried in a vacuum oven at 60°C under a pressure of 0.01MPa. The obtained powders were sintered by hot-pressing (Model: HIGH-MULTI, 5000, Germany) at 1450°C under a sintering pressure of 20 MPa. Considering the transformation of PANf into carbon fibers, the sintering process was optimized as Figure 1. The sintering temperature was maintained at 600 and 1100°C for 5 min and the pressure gradually increased to 20 MPa after the temperature reaching 600°C. After sintering, the specimens were ground mechanically and cut into rectangular bars by electrical discharge machining. After that, the bars were polished with diamond papers to mirror surface with a dimension of about 3 × 4 ×35 mm3.
2.2. Materials characterization

The density of the samples was measured by Archimedes method according to international standard (ISO 18754). The relative density was defined as the percentage of the apparent density to their corresponding theoretical density. The hardness ($H_{V_{10}}$) was evaluated on a Vickers hardness tester (Tukon-2500, Wilson Wolpert Co. Ltd., America) with a load of 98 N (10 kgf) and a dwell time of 15 s. The flexural strength was measured by a three-point bending method on an AG-IC20 kN Shimazutester with a span length of 30 mm and a loading rate of 0.5 mm/min. The fracture toughness ($K_{IC}$, MPa·m$^{1/2}$) was calculated by measuring the crack length near the indent resulted from the hardness test, according to the Shetty equation [21]:

$$K_{IC} = 0.0889\sqrt{HV}\frac{P}{\sum l_i l_i}$$

where $HV$ is the Vickers hardness (N/mm$^2$) of the samples, $P$ the load (N) during indentation, and $l_i$ the length of the $i^{th}$ crack emerging from the hardness indent ($\mu$m).

In addition, the phase identification was performed by X-ray diffraction (XRD, Model: D8-Advance, Germany) with Cu Kα radiation ($\lambda=1.54178$ Å) through a continuous scanning mode at a speed of 5 °/min. The microstructure examinations on the fresh fractured, etched and polished surfaces of the samples were carried out by a scanning electron microscope (SEM, Model: JSM-7001F, Japan) equipped with an energy-dispersive X-ray (EDX) spectrometer. The cracks around the Vickers indentations were also observed. The etching of the samples was carried out in a Murakami’s reagent (1 g potassium ferricyanide, 1 g potassium hydroxide and 10 g water).

3. Results and discussion

3.1. Phase composition and microstructure

Figure 2 shows the SEM images of the WCVP-0 and WCVP-2.0 composite powders after ball milling. It can be seen that the WCVP-0 composite powder has a relatively homogeneous particle size distribution (see Figure 2a) with a mean size of ~0.4 μm (see the inset in Figure 2a). In the WCVP-2.0 composite powder, the PAN$_f$ and WC-Co powders were relatively homogeneously dispersed without the agglomeration of the PAN$_f$ after long time ball milling (see Figure 2b). The mean length of the PAN$_f$ was about 50 μm with the mean diameter of ~5 μm. It was observed that some ultrafine particles (about 0.2 μm) were coated on the PAN$_f$ in the magnified image (see the inset in Figure 2b). In addition, the mean particle size of WC and the length of the PAN$_f$ decreased due to the long time ball milling.
Figure 2. SEM images of the initial powders. (a) WCVP-0 powder (inset: particle size distribution), and (b) WCVP-2.0 powder (inset: magnified image for the selected area).

Figure 3. XRD patterns of the sintered samples with different contents of PAN$_f$.

Figure 3 displays the XRD patterns of the sintered cemented carbide samples with different contents of PAN$_f$. In all the samples, WC phase (JCPDS PDF card: 65-8828) was detected, and Co and carbon phases were not identified in the detection limit of XRD. However, the η phase, a complex carbide phase (M$_6$C, normally consists of Co$_2$W$_4$C and Co$_3$W$_3$C) was detected in the samples with 0 to 1 wt.% PAN$_f$ addition due to their states of significant carbon deficiency. The present result indicated that the C content in the samples with no more than 1.5 wt.% PAN$_f$ addition was significantly lower than that in stoichiometric WC. And because the Co solubility in WC is extremely small (≤0.5 at.%), so the formation of η phase depends on the dissolution of WC in Co. And in the ternary Co-W-C system, the η phase is stable when the samples have higher W content in Co [22]. What’s more, with the increase in the added fraction of PAN$_f$, the corresponding 2θ of η phase shifted to a higher degree. The calculated lattice parameter of the η phase gradually decreased from 11.17048 to 11.11875 Å, falling in between the lattice parameters of Co$_2$W$_4$C and Co$_3$W$_3$C phases, as shown in Table 2. And the relative intensity of η phase gradually decreased with increasing addition fraction of PAN$_f$, which could even not detected in the samples added with 1.5 and 2 wt.% PAN$_f$. These results reveal that the added PAN$_f$ may be in situ transformed into carbon fiber during sintering and the formed carbon fiber
supplied carbon to the system, resulting in the less W dissolved in Co and thus the relative intensity of the \( \eta \) phase decreased. The reduction of the \( \eta \) phase was beneficial to the enhancement of the density and Vickers hardness of the sintered samples.

Table 2. Lattice parameter \( a \) and XRD relative intensity of the \( \eta \) phase (cubic phase) in the samples with different fractions of PAN\(_f\).

| Samples       | Co\(_2\)W\(_4\)C | WCVP-0 | WCVP-0.5 | WCVP-1.0 | Co\(_2\)W\(_4\)C |
|---------------|-----------------|--------|----------|----------|-----------------|
| lattice parameter \( a \) (Å) | 11.21 | 11.17048 | 11.12302 | 11.11875 | 11.112 |
| XRD relative density | - | 8.2 % | 6.7 % | 4.3 % | - |

Figure 4 shows typical second electron (SE) SEM images on the etched surface of the sintered samples and typical grain size distribution. It can be seen that the added PAN\(_f\) presented no significant effect on the grain size of the samples and the mean grain size of typical sample WCVP-0 was about 0.45μm. It can be safely concluded that ultrafine fine WC-Co cemented carbides have been obtained in this work due to the small applied amount of Co in the present samples.

![Figure 4](image)

**Figure 4.** Typical SE-SEM images on the etched surface of the sintered samples with different contents of PAN\(_f\); (a) WCVP-0, (b) WCVP-1.0, and (c) WCVP-2.0. And (d) the grain size distribution in sample WCVP-0. The samples were etched in Murakami’s reagent for 2 min.

Figure 5 exhibits typical back-scattering (BS) SEM images on the polished surfaces of the sintered samples with different contents of PAN\(_f\). It could be observed that without PAN\(_f\), there were many micro-pores in the obtained sample. The phase composition analysis presented above already indicated that without PAN\(_f\), \( \eta \) phase was formed due to the carbon deficiency in the sample. Because the formation of \( \eta \) phase would consume the binder phasem thus suppressing the densification of cemented carbides, so a lot of micro-pores existed in the sample WCVP-0. The surface of the sample with 1.0 wt.% PAN\(_f\) was relatively smoother than that of the sample without PAN\(_f\), and less pores
could be observed in it. Because carbon fiber could not be observed in this sample, it is reasonable to assume that the formed carbon fiber had reacted with the raw powder, supplying carbon in the sintering system. In the sample with 2 wt.% PAN, even lesser micro-pores could be observed in the sample, and a lot of short black fibers could be examined on the surface. EDX analysis was carried out on the gray and black zones in the sample, and typical results are presented in Table 3. It was revealed that in the black zones, the atomic percentages of carbon and tungsten elements accounted for 99.54% and 0.31%, but in the gray zones, they were 76.18% and 22.23%, respectively. This result indicated that the added PAN had been in situ transformed into carbon fiber. But due to the reaction between the carbon fiber and η phase, the fiber might not keep its shape and/or become non-intact.

![Figure 5. Typical BS-SEM images on the polished surfaces of the sintered samples with different contents of PAN](image)

| Table 3. EDX results in different zones as shown in Figure 5c |
|-------------------------------------------------------------|
| Elements (at.%) | Spectrum 1 (black) | Spectrum 2 (gray) |
|-----------------|--------------------|-------------------|
| C               | 99.54              | 76.18             |
| V               | 0.06               | 0.87              |
| Co              | 0.08               | 0.72              |
| W               | 0.31               | 22.23             |

Figure 6 illustrates the apparent and relative densities of the samples with different addition fractions of PAN. The relative density was defined as the percentage of the apparent density to their corresponding theoretical density. And here the theoretical density was calculated according to the mixed rules with the assumption that all the added PAN had been transformed into carbon fibers. It can be seen that with increasing addition fraction of PAN into the samples, the apparent density increase first and then decrease, presenting a maximum when 0.5 wt.% PAN was added. The decrease in apparent density can be easily understood because the density of in situ transformed carbon fiber is
lower than any of components in the samples. But the increase in apparent density surely indicates that the formed carbon fiber was beneficial to the densification of the samples, which can be confirmed by the relative density variation with the added fraction of PAN\textsubscript{f}. The relative density of the samples gradually increased from 86% to 95% with the increase in the added fraction of PAN\textsubscript{f} from 0 to 2.0 wt.% which is also consistent with the results from SEM observation. The improved densification of the samples after the addition of PAN\textsubscript{f} can be attributed to the reduction of the \(\eta\) phase by the in situ transformed carbon.

![Figure 6. The apparent and relative densities of the samples with different addition fractions of PAN\textsubscript{f}.](image)

![Figure 7. SE-SEM images on the fractured surface of the sintered samples with different addition fractions of PAN\textsubscript{f}}: (a) 0, (b) 0.5 wt.%, (c) 1.5 wt.% and (d) 2.0 wt.%.](image)
3.2. Mechanical properties

Figure 7 shows typical SE-SEM images on the fractured surface of the sintered samples with different addition fractions of PAN$_f$. Because of the less content of binder phase left due to the formation of Co$_3$W$_3$C phase, many micro-pores can be observed on the fractured surface of the sample without PAN$_f$ (see Figure 7a), which is consistent with the morphology on its polished surface. With 0.5 wt.% PAN$_f$ addition, less micro-pores can be observed on the fractured surface and many ridges would form during the fracture (see Figure 7b). But no in situ formed carbon fiber can be examined on the surface. With 1.5 wt.% PAN$_f$ addition, much of the in situ formed carbon fiber can be observed on the sample surface. The formed carbon fiber could deflect the direction of crack propagation during the fracture, resulting in a cross section on the fracture surface as shown in Figure 7c. That phenomenon implies that the in situ formed carbon fiber can absorb the fracture energy during fracture, and thus strengthen the cemented carbide. In the sample with 2 wt.% PAN$_f$ addition, more of in situ formed carbon fiber can be examined on the sample surface and the pull-out of carbon fiber can be easily observed (see Figure 7d).

Figure 8 illustrates the Vickers hardness, three-point bending flexural strength and Palmqvist indentation toughness of the sintered samples with different addition fractions of PAN$_f$. With the increase in the added fraction of PAN$_f$, the Vickers hardness of the samples initially increased and then decreased, reaching its maximum value (about 1900 HV$_{10}$) for the sample with 0.5 wt.% PAN$_f$ addition. The hardness of cemented carbides mainly depends on the hard phase content, relative density and grain size. The variation of grain size with the added fraction of PAN$_f$ into the present samples contributed very little to the hardness, because the effect is not significant (see Figure 6). Therefore, the main factor affecting the hardness should be the hard phase content and relative density. With 0.5 wt.% PAN$_f$ addition, the in situ formed carbon fiber reacted with Co$_3$W$_3$C phase and thus the
relative density of the sample would be improved, and the variation of hard phase content was not obvious, finally resulting in the improvement of Vickers hardness. However, with more PANf addition, more and more carbon fiber formed in the sample. Because the hardness of the carbon fiber was much lower than that of cemented carbides, as their volume content increased, the hard phase content in the samples decreased, resulting in gradually decreased hardness, although the relative density of samples would be increased. And just because of the improvement in relative density, the hardness of the sample with 2 wt.% PANf was still higher than that of the sample without PANf addition.

With the increase in the added fraction of PANf, the flexural strength of the samples gradually increased. The flexural strength of cemented carbides mainly depends on the relative density of the samples. The micro-pores would form the cracks during the fracture. As seen in Figures 5 and 7, lots of micro-pores can be observed in the sample without PANf, resulting in the lowest flexural strength in all the samples. With the addition of PANf, the relative density of the sample increased, which was beneficial to the improvement of flexural strength. Moreover, the formed carbon fiber would react with Co-W-C to form more Co, which would enhance the bonding strength among the WC grains. During fracture, more ridges would be observed on the fractured surface as shown in Figure 7b. With more PANf addition (more than 1 wt.%), many in situ transformed carbon fiber can be observed in the samples. During fracture, the fibers would absorb more fracture energy, finally improving the flexural strength of the samples, as seen in Figure 7c and d.

![Cracks deflection](image1)

![fiber bridging](image2)

![Ending of crack](image3)

**Figure 9.** Typical SE-SEM micrographs of the cracks around Vickers indentations on the samples with 2 wt.% PANf.

With the increase in the added fraction of PANf, the fracture toughness of the samples gradually increased. The improvement of the fracture toughness with the increase in the added fraction of PANf can be attributed to the increase in relative density and the formation of carbon fiber. With no more than 1 wt.% PANf, the effect of in situ transformed carbon fiber was not significant as seen in Figure 5 and 7. In this case, the improvement in relative density would be the main factor for the improvement of fracture toughness. With more addition of PANf (more than 1 wt.%), more and more carbon fiber
formed and retained in the samples. The carbon fiber would suppress the propagation of cracks during fracture. Figure 8 displays typical SEM micrographs of the cracks around the Vickers indendations after hardness measurement on the sample with 2 wt.% PANf addition. The pull-out of fiber, crack deflection and fiber-bridging can be observed in Figure 9a and b, which will consume more energy during fracture. The propagation of cracks would even end at the fiber (see Figure 9c). Therefore, the fracture toughness of the sample gradually increased with the increase in the added fraction of PANf in the present content.

4. Conclusions
WC-2Co cemented carbides toughened by in situ transformed carbon fibers were prepared by hot-press sintering at 1450°C using pre-oxidized PAN fibers as the precursor. The in situ transformed carbon fiber could supply carbon to the sintering system to suppress the formation of Co3W6C phase and improve the relative density of the samples. With the increase in the added fraction of PANf, the Vickers hardness initially increased and then slightly decreased, reaching its maximum of about 1900 HV10 for the sample with 0.5 wt.% PANf. The flexural strength and fracture toughness of the samples gradually increased from 530 MPa and 5.5 MPa·m1/2 to 700 MPa and 7.5 MPa·m1/2 respectively with the increase in the added fraction of PANf from 0 to 2 wt.%. The toughening mechanisms were cracks deflection, fiber pull-out and crack bridging.

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