Fibrous nano composite reinforced surface on WC-Co cemented carbide achieved by pulsed electron beam irradiation and subsequent tempering

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Abstract. Exotic microstructures can be tailored by extreme conditions with combined material processing techniques for desirable properties. In this work, an innovative 2-staged process was explored for WC-10Co cemented carbide surface modification. Firstly, rapid thermal cycles were induced by high current pulsed electron beam (HCPEB) irradiation at energy density of 6 J/cm², during which the micro-WC/Co was melted and re-solidified into a nano-scaled equiaxed grain microstructure with metastable fcc-WC_{1-x} as the majority phase in the surface layer (~2 μm). Thereafter, a subsequent tempering process was applied to the HCPEB-irradiated cemented carbide specimens and the nano equiaxed grains in the surface layer were gradually transferred into nano-scaled fibrous microstructure. Phase transformation was investigated using thermo-gravimetric analysis differential scanning calorimetry (TGA-DSC), confocal laser scanning microscopy (CLSM), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Analysis showed that the fibrous nano structure resulted from the decomposition of WC_{1-x} at 600-700 °C via fcc-WC_{1-x} → hex-WC + hcp-W₂C. After the 2-staged process, the surface microhardness was greatly improved.

1 Introduction

Cemented tungsten carbide holds excellent mechanical properties such as high hardness, fracture strength and wear resistance, thus, has been widely used as drilling, cutting, machining tools[1,2]. To extend applications as a tool material and service span for

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high-speed/precision machining, further improvement of mechanical properties by surface optimization is highly demanded and favorable for cemented carbide [3]. To date, two main approaches of technical measures were utilized to optimize the surface condition of the WC-based cemented carbide surface[1,4,5]. One is to fabricate nanostructured cemented carbide bulks by improving the sintering process. The other is to fabricate a protective layer on the surface.

In recent years, high current pulsed electron beam (HCPEB), among other energetic beams, has been fast developed as a unique surface modification technology[6-9]. HCPEB irradiation can generate an extreme thermal field (large heating rate $\sim 10^{8-10}$ K/s and large cooling rate $\sim 10^{8-9}$ K/s) in the surface area of the target material, where a tailored surface layer ($\sim \mu\text{m}$) composed of nano-grained microstructure can be achieved[10-14]. Considering the metastability of the HCPEB-induced microstructure, it is possible that with proper post-HCPEB thermal treatment, this modified surface would undergo a series of solid state phase transformations, resulting in the formation of a surface layer at more stable state with further enhanced property. In this study, WC-10Co cemented carbide was subjected to a 2-stage process, i.e., HCPEB irradiation and the subsequent tempering treatment. A nano fibrous composite was formed on the surface of the cemented carbide after the 2-stage process. Microstructure evolution was analyzed to elucidate the mechanism of the solid-state phase transformation leading to the formation of the fibrous composite surface.

2 Materials and methods

Cemented carbide WC-10Co bars were machined by wire cut electrical discharge cutting) into cylinders ($\Phi 15 \text{ mm} \times 8 \text{ mm}$) as specimens. The composition of the cemented carbide is 10 wt. % Co and WC rest. The typical microstructure of the cemented carbide and the corresponding XRD spectrum are shown in Fig. 1. Angular shaped WC grains with an average grain size of $\sim 1.2 \mu\text{m}$ are bonded by the Co phase. Prior to treatment, one basal plane for each specimen was mechanically ground by diamond disks up to 1200#, and then ultrasonically cleaned in acetone.

Fig. 1. SEM image(a) and XRD(b) of WC-10Co cemented carbide.

The 2-stage treatment process was illustrated in Fig. 2. A HOPE-I type pulsed electron beam apparatus [6] was used for the irradiation; working parameters in this work are listed as Table 1. The specimens were firstly irradiated with pulse number $N=1, 6$ and 20 . The phase composition of the WC-10Co cemented carbide changed greatly after HCPEB irradiation (Fig. 3). When $N=6$ and 20 , the WC_{1-x} phase became predominant in the surface layer, where some minority phases such as W_2C , graphite were also identified.

Fig. 2. Schematic illustration of the 2-stage process.

Table 1. Working parameters of the HCPEB irradiation used in the present work.

Accelerating voltage (kV)	Pulse duration (μs)	Pulse interval (s)	Energy density (J/cm ²)	Vacuum (10 ⁻³ Pa)	Specimen-anode distance (cm)
27	2.5	30	6	6.5	10

The exothermal feature in TGA/DSC analysis indicated the favorable temperature range for phase transformation to be about 600 to 1200 °C (Fig. 4). After primary evaluation, 6 and 20 pulses irradiated specimens were selected for tempering treatment. A GSL-1500X-OTF vacuum tube furnace (heating rate 10 °C/min designated) was used for the tempering process of the HCPEB-irradiated specimens with Ar protection. Tempering temperature (TT) was chosen as 500, 600 and 700 °C. The furnace temperature was held constant for 1 h after thermal ramping, and then cooled down to room temperature within the furnace.

Fig. 3. XRD of WC-10Co cemented carbide irradiated with 1, 6 and 20 pulses of HCPEB.

Fig. 4. DSC/TGA signals of WC-10Co cemented carbide irradiated with 1, 6 and 20 pulses.

The phase identification was carried out in an X-ray diffractometer (Shimadzu XRD-6000) with Cu-K α radiation. Thermo-gravimetric analysis differential scanning calorimetry (TGA-DSC) was carried out for using a simultaneous thermal analyzer (METTLER TOLEDO TGA/DSC 3+), under Ar gas flow with a heating rate of 10 °C /min. The microstructure of the specimens was analyzed using a field emission scanning electron microscope (Zeiss Supra55 SEM). Surface microhardness was measured with a Vickers indentation tester (Huayin HV-1000A) at a load of 25 g.

3 Results and discussion

Fig. 5 shows the modified microstructure of the specimens treated at different stages. The HCPEB irradiation induced drastic microstructure changes. When N=6, a remelted layer ($\sim 2 \mu\text{m}$) formed, composed of nano-grained (30-100 nm) microstructure (mainly WC_{1-x} phase) with black particles (graphite). When N=20, the nano grained microstructure became more refined and homogeneous (30-50 nm), graphite particles disappeared. Tempering at 500 °C affected little on HCPEB-induced surface microstructure. After tempered at 600 °C, a swelling aspect showed on the N=6 surface in parts. After tempered at 700 °C, fibrous microstructure formed ($\sim 20 \times 100 \text{ nm}$). Microstructure change for the N=20 surface resembled feature on the N=6 surface, but the fibrous microstructure was more coarse ($\sim 40 \times 300 \text{ nm}$) and organized.

Fig. 5. Typical SEM images of WC-10Co specimen: the surface (a) and cross-sectional view (b) of 6-pulsed, after tempering at 600 °C (c) and 700 °C (d); the surface of 20-pulsed (e) and after tempering at 700 °C (f).

Fig. 6 shows the XRD spectrums of the post-tempering specimens. Phase transformations were similar for N=6 and N=20 specimens. Obvious changes appeared when TT was elevated to 600 °C, as the peak intensity of the fcc-WC_{1-x} phase decreased while that of the hex-WC and hcp-W₂C phases increased. The WC_{1-x} phase faded away after tempered at 700 °C. Several points should be highlighted: ① un-indexed peak pairs (noted with black arrows) on the spectrums of the specimens tempered at 600 and 700 °C should be corresponded to two transitional phases (TPs) which are considered beneficial for reducing the resistance of solid-state phase transformation. ② When tempering temperature was elevated from 500 °C to 600 °C, the peaks of the WC_{1-x}, such as (111) and (200), shifted slightly to higher angles, which is related to the lattice distortion.

Fig. 6. XRD patterns of HCPEB-irradiated WC-10Co cemented carbide after tempering treatment: (a) 6 pulse irradiated, (c) 20 pulse irradiated; (b) and (d) the corresponding local enlargements.

Surface microhardness of the WC-10Co cemented carbide before and after treatment at different stages is given in Fig. 7. Improvement of microhardness was shown for all treated WC-10Co cemented carbide specimens. For the irradiated WC-10Co cemented carbide specimen, the N=20 surface (25.9 GPa) was much harder than the N=6 (20.5 GPa). After tempering treatment at 500 °C, the N=6 surface was hardened while the N=20 surface softened, indicating that the tempering treatment neutralized the advantage in the N=20 surface. Further elevating the tempering temperature, microhardness increased and reached maximum values at 700 °C for both N=6 and N=20 (24.8 and 24.0 GPa, respectively).

Fig. 7. Microhardness of WC-10Co cemented carbide before and after tempering.

Two main factors contribute to the surface microhardness change of the WC-10Co cemented carbide at different stage processes: i) the grain refinement strengthening which is also seen in other HCPEB irradiated metals and alloys [6-9], ii) the formation of the nano-scaled fibrous composite structure aroused by the subsequent tempering treatment (at 700 °C). As for specimens tempered at 500 °C, the process can be considered as annealing since no phase transformation occurred. An annealing hardening was observed for the N=6 surface; similar cases were seen in other nano crystalline materials [15]. However, after same tempering treatment, the N=20 surface was softened. Considering the grain size difference in as irradiated states, the existence of grain size threshold for annealing hardening is indicated.

4 Summary

The main results can be generalized as follows:

(1) HCPEB irradiation with energy density at 6 J/cm^2 induced rapid melting-solidification cycles in the surface layer ($\sim 2 \text{ }\mu\text{m}$) of WC-Co cemented carbide, leading to the formation of nano-scaled equiaxed grained microstructure, where the metastable WC_{1-x} was identified as the majority phase.

(2) The subsequent tempering activated decomposition of the HCPEB-induced nano- WC_{1-x} , resulting in the formation of the nano fibrous composite (mainly WC and W_2C phases) in the surface layer. The grain size on N=20 surface was larger than that on the N=6 surface. The formation of WC phase appeared favorable during the solid-state phase transformation.

(3) The treated specimens exhibited higher microhardness. The improvement of surface hardness was mainly ascribed to grain refinement strengthening, the formation of the nano fibrous phases.

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