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1	The process of surface carburization and high temperature wear behavior of
2	infiltrated W-Cu composites
3	
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14	
15	Abstract
16	Tungsten-copper (W-Cu) composites are used as high temperature frictional
17	materials under special service conditions for electromagnetic gun rail and precision
18	guide for rolled pieces due to their good ablation resistance and electrical conductivity.
19	However, they have poor wear resistance at elevated temperatures. In this paper, surface
20	carburization method was applied on the W-20wt.%Cu composite to investigate the
21	mechanisms of carburization and its effects on the high temperature friction behavior

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of composite. Carburization process has been done at a temperature of 1100 °C for 30 1 hours. The obtained results showed that carburizing at 1100 °C with a dwelling time of 2 3 30 hours resulted into formation of a carburized layer and a dense intermediate sublayer on the substrate. Also, the surface carburized layer with a thickness of about 70 4 µm composed of mixed phases of graphite, WC and W2C. The hardness of carburized 5 layer (~HV454) was significantly higher than that of substrate (HV223). Also, bending 6 7 and[S1] strength of the carburized W-Cu composites has been significantly improved, although their electrical conductivity and tensile strength was decreased slightly. The 8 9 carburization mechanism of the W-Cu composites was found to be dominant by carbon atom diffusion through reaction with W atoms and formation of surface liquid copper, 10 which promoted migration and diffusion of tungsten and carbon at high temperatures. 11 12 Average coefficients of friction and wear rate of carburized W-Cu composites are all lower than these of un-carburized W-Cu composites owing to the presence of surface 13 14 carburized layer. Also, formation of CuWO₄ at high temperatures reduced the friction and wear resistance of the W-Cu composites. 15

16

17 Keywords: W-Cu composites; Carburizing; Microstructure; Friction and Wear

18

19 **1. Introduction**

Tungsten copper (W-Cu) composites is a non-miscible pseudo-alloy which consist of mixed W and Cu phases and is generally produced using a powder metallurgy technology [1-2]. It has numerous good properties, such as good resistance to arc erosion, good machinability, relatively high strength, and good thermal conductivity, thus has been widely used in electronic seals, high-voltage electrical contacts [3],

electromagnetic railway [4], nozzle throat for rocket engine [5] and oval hole guide for 1 the precision rolling mill [6-7]. However, failure of components during service was 2 3 frequently initiated from the surface of the composites components, especially when there are various types of surface defects [8-9]. Due to the lower melting point and 4 cooling effect of Cu and the high melting point and high strength of W, W-Cu 5 composites generally show a good performance when they are used as guides and 6 guarding materials. However, they often show premature failures due to their 7 insufficient surface hardness [10]. Therefore, Liu et al. [11] have been reported using 8 9 of different methods to improve the surface properties of the W-Cu composites, which 10 include surface coating, nanoscale surface sputtering, and surface diffusion processes such as carburization or nitriding. 11

12 Surface carburization is widely used in many industries because the process is simple and there is no need for expensive equipment and complicated processes. The 13 process has been traditionally used for iron-steel materials, but recently been extended 14 15 to titanium and titanium alloys, tungsten alloys, zirconium alloys and other non-ferrous metal materials. For example, He et al. [12] reported that carburization of Ti-48Al-2Cr-16 2Nb alloy could be achieved at 920 °C with a dwelling time of 2 hrs. A uniform and 17 dense carburized layer was generated on the surfaces of TiAl alloys, and their anti-18 19 oxidation and mechanical properties were significantly improved. Li et al. [13] reported 20 that hydrogen-free glow-discharge plasma carburizing of titanium could be conducted in a vacuum of 5×10^{-3} Pa and 99.999% Ar atmosphere. Results showed that the depth 21 of carburized layer was more than 100 µm and the Vickers hardness was ~ 612 HV with 22 23 a friction coefficient of 0.11. Wang et al. [14] investigated carburization of Ti based composites and formation of TiC layer on the α-Ti substrate and reported that the 24 carburization of a high-density tungsten alloy could be achieved at 950 °C for 5 hrs. 25

The thicknesses of surface W_2C layer were in the range of 170 µm to 200 µm and the hardness values were varied from HV 388 to HV 525. This treatment had effectively improved the surface hardness of armor piercing bullets, whereas the core of the projectile could be easily broken under a high-speed impact, thus improving its selfsharpening performance and enhancing its piercing ability, which was reported by Jung et al. [15].

However, to the best of our knowledge, there is no any report on the study of the
carburization behavior and mechanism of W-Cu composites so far, experimentally or
theoretically. In the present study, we will focus our work on solid carburization of the
W-20wt.% Cu composites and for the first time; identify their behavior against high
temperature friction and wear.

12

13 **2. Experimental**

The W-Cu composites used in this work were fabricated by infiltrating the molten copper into a tungsten porous skeleton. Chen et al. [16] described the detailed preparation process. The nominal weight fractions of W and Cu were 80 wt% and 20 wt%, respectively. The basic properties of the composite materials are listed in Table 1.

19 Table 1 Physical and mechanical properties of W-Cu composite used in the work.

20

The specimens of the W-Cu composites were firstly machined into the form of a cylinder with a dimension of $\Phi 60 \text{ mm} \times 30 \text{ mm}$. The surfaces of samples were carefully polished using 240-grade abrasive sandpaper. The sample was embedded inside graphite powders with an average particle size of 150~200 mesh, while 10% sodium carbonate was added as a penetration agent. The buried sample in the graphite powders was placed in an atmospheric carburizing furnace under flowing H₂ atmosphere and

1	heated to the temperatures of $1100\pm10^{\circ}$ C, the carburization temperature was
2	controlled using a high temperature infrared thermometer (Smart, AS892). The heating
3	rate was 10 °C/min and the holding time at soaking temperature was 30 hours. After
4	carburization, the furnace was cooled down to room temperature.
5	
6	Fig. 1 Schematic of the carburization experiments for W-Cu composites.
7	
8	The friction test was done on the carburized sample and un-carburized composites.
9	This test was carried out using an HT-100 pin-on-disc high temperature wear tester. The
10	test condition was dry friction at a high temperature of 900 °C with normal loads of 5
11	N and 20 N. The sliding speed during wear testing was 300 r/min. The size of testing
12	sample (i.e., pins) was a diameter of 5 mm and a height of 10 ~ 12 mm. A gray cast iron
13	(HT 250 with a hardness of HB 190) with a diameter of 50 mm and a height of 5 mm
14	was chosen as frictional counterpart. And then the wear rate of W-Cu composites is
15	measured using a MicroXAM 3D surface profilometer system to determine the wear
16	volume. The detailed measured process had been reported by author Xu et al. [17].
17	Microstructures and fracture morphology of the samples before and after
18	carburization were observed using a scanning electron microscope (SEM, JSM-6700).
19	The chemical elements were analyzed using an energy dispersive X-ray spectroscopy
20	(EDS) and electron probe microanalyser (EPMA) analyzer attached with the SEM.
21	Crystalline structures of the carburized samples were analyzed using an X-ray
22	diffractometer (XRD, XRD-7000S, Cu K-alpha radiation), with a scanning rate of
23	8 °/min, a scanning range of 2 θ of 10 ~ 90 ° and a step size of 0.02°. The different layers

of carburized samples were tested using a layer-by-layer delamination method. The
 carbon and oxygen concentrations at the different positions of the carburization layer
 were measured using EPMA.

Mechanical properties of samples before and after carburization treatment were characterized with a three-point bending method using a HT-2402 universal test machine. The size of sample was 5.25 mm × 9.97 mm × 24.6 mm. The bending strength was calculated according to the following equation [18]:

8
$$\sigma_r = \frac{3FL}{2bh^2}$$
(1)

9 where σ_r is bending strength (MPa), *F* is the maximum load during fracture (N), *L* is 10 spacing between two lower supporting points (mm), *b* is specimen width (mm), and *h* 11 is specimen thickness (mm). The tensile test was carried out at room temperature at a 12 strain rate of 1 mm/min using a WE-100 universal tester. The hardness of the samples 13 was measured using a micro-Vickers hardness tester (TUKON2100), and the applied 14 load was 200 g with a holding time of 10 s. The electrical conductivity of the samples 15 was measured using a metal electrical conductivity tester (D60K).

16

17 **3. Results and discussion**

In order to verify that the surface of the W-Cu composites was covered with carbon-rich layer, cross-section microstructures of the W-Cu composite after carburization at 1100 °C were observed using SEM (Fig. 2(a)). Cross-section morphology of the W-Cu composite after carburization is composed of three distinct regions, as shown in Fig. 2(a) (i.e., the loose surface layer; a dens intermediate layer on the substrate). The first loose layer is attributed to various reasons during high

1	temperature process, such as accumulation of graphite powder, formation of voids due
2	to the partial bonding at high temperature, and channel formation created by
3	evaporation of liquid copper on the surface. Carbon concentration distribution of W-Cu
4	composite after carburization at 1100 °C for holding time 30 h was exhibited in Fig.
5	2(b), in which the C atom have diffused into the W-Cu matrix. Also, SEM images and
6	elemental mapping analysis results from surface morphology of the W-Cu composites
7	before and after carburization at 1100 °C are shown in Fig. 3. In Fig. 3(a1), the gray and
8	black areas are W and Cu phases, respectively. Also, the SEM image of the
9	uncarburized W-Cu composites reveals compact and smooth. And the Cu phases are
10	homogeneously distributed around the W phase, as observed in Figs. $3(a_2) \sim 3(a_4)$. As
11	illustrated, after carburization (in Fig. 3(b)), the surface of carburized W-Cu composites
12	(especially W particles) exhibits many edges and corners which are quite rough. There
13	are a large number of small W particles around the Cu phases. It can also be found that
14	the volume fraction of the binder phase or porosity (the dark/black area in Fig. 3(b))
15	increased significantly because the edges and corners of the W particles are dissolved
16	by the binder phase of Cu in the activation of carbon was reported by Huang [18]. It is
17	also possible that W reacts with carbon to form carbide. In order to determine the phase
18	presence and C distribution in the surface of the carburized W-Cu composites, energy
19	dispersive spectroscopy (EDS) analysis was also perform on the entire surface in Fig.
20	3(b), the results are shown in Fig. 3 (b ₁) ~ $3(b_4)$. We can found that C atom are
21	distributed on the grain boundaries of W or Cu grains, especially most of C atoms are
22	covered around the W particles, the main reason is that C can be easily transported in

1	the form of hydrocarbons over a distance of several millimeters up to centimeters on
2	the W-matric composites when they are in the condition of H_2 atmosphere [19]. The
3	precious presence and content of carbon inside the carburized W-Cu composites is
4	identified from the EPMA analysis, as shown in inset of Fig. 3(b5), indicating the
5	reactions between tungsten and carbon are happened. Also, compared Fig. 3(a2) with
6	3(b ₂), the Cu and W element distribution in W-Cu composites changed a lot after
7	carburization at 1100°C owing to the formation of carbide and the flowing and
8	solidification of liquid Cu. At the same time, evaporation and spillover of copper cause
9	a decrease in copper content of the surface during high temperatures carburization, as
10	shown inset of Fig. 3(a) and 3(b ₅), the copper concentration reduced from 18.87wt.%
11	to 13.94wt.% in the surface layer after carburization. The W particles in the
12	intermediate layer become no longer smooth compared to those in the matrix layer after
13	carburization, and there are many edges and corners, accompanying with a large
14	number of small tungsten particles surrounding the Cu phases, which is consistent with
15	the results shown in Fig. 3(b). From the EPMA analysis of carbon distribution shown
16	in inset of Figs. 3(a) and 3(b ₅) (i.e. as shown in the inset tables of these figures), the
17	surface carbon content is higher than the sub-surface carbon content. With the increase
18	of distance from the exposure surface, the carbon content reduces, and finally decreases
19	to zero in the substrate. The result verifies that the carbon elements were diffused into
20	the substrate, and the carburized layer was formed with a thickness of about 40~80
21	microns. [S2] Combined with Fig. 4(b), the obvious diffusion of C between 100 \sim 200
22	μ m can be observed,, which revealed the average carburized layer is about 70 μ m.

- 1
- 2

Fig. 2 (a) SEM morphology from cross section and (b) carbon concentration distribution ofW-Cu composite after carburization at 1100 °C for holding time 30h.

4 5

Fig. 3 SEM surface morphologies and EDS results of W-Cu composites (a, a₁, a₂, a₃) before carburization and (b, b₁, b₂, b₃, b₄, b₅) after carburization at 1100°C, respectively.

6 7

The composition and microstructures of the W-Cu composite (in Fig. 2) show three 8 different characteristic regions after carburization treatment. This is mainly because the 9 10 composite was buried inside graphite, and there is a carbon concentration gradient formed into the sample. Increase of the surface carbon content will reduce the liquid 11 12 phase formation temperature of the composites was reported by Liu et al. [20], which 13 results in an early formation of the liquid phase of composites at the surface. Carbon atoms react with tungsten to form the WC or W_2C , through dissolving and precipitation 14 15 of newly formed WC particles, and also through the formation of liquid copper phase on the surface. Because carbon and tungsten atoms have a large affinity at high 16 temperatures, the C atoms could migrate inward and then react with W atoms to form 17 18 the WC or W₂C. Therefore, the surface content of W decreases, and the outward migration of W to the surface leads to the formation of volume vacancy at reaction sites 19 [21]. This will drive the surface liquid copper to migrate inwards to fill up the volume 20 21 vacancy due to the tungsten's outward migration. Therefore, the outward migration of 22 the W atoms and the inward migration of liquid copper simultaneously occur in the carburizing process of the W-Cu composites. 23

Fig. 4(a) is a back-scattered electron image of the carburized W-Cu composites, indicating that the W (green dots) and Cu (red dots) phases are homogeneously distributed inside the matrix. Carbon elements (dark dots) are distributed along the

1	cross-section of the composites, and the EDS elemental line scan is shown in Fig. 4(b).
2	It can be seen that the copper and tungsten are diffused outward, whereas the carbon is
3	diffused from outside into the composites, on the other hand, the curve oscillation for
4	Cu concentration in Fig. 3(b) is attributed to the melting and flowing during the
5	carburization process, which further validates the previous analysis (Fig. 3).
6	
7	Fig. 4 (a) SEM mapping image and (b) elemental line scan curves of surface carburized W-Cu
8	composite.
9	
10	Fig. 5 shows the XRD patterns at different cross-section positions of W-Cu
11	composites after carburization. It can be seen that at the center of the tungsten-copper
12	composites, only the W peak (cf JCPDS file No. 04-0806) and Cu (cf JCPDS file No.
13	04-0836) peak are detected. After carburization, the surface layer shows the phases of
14	WC (cf JCPDS file No. 51-0939), W ₂ C (cf JCPDS file No. 20-1315) and graphite or C
15	(cf JCPDS file No. 50-0926). According to the W-C phase diagram [22], tungsten
16	carbides generally have three phases of WC, W_2C and WC_{1-x} . In this study, WC_{1-x} was
17	not detected in the surface and sub-surface. This is because the WC_{1-x} is a high-
18	temperature metastable phase [23] which is easily decomposed into W_2C , WC and W
19	phases during the slow cooling process. Therefore, the carbides on the surface of the
20	carburized specimen are WC and W2C. In addition, the carbon peak can also be detected
21	in the surface layer, which is related to diffused C without reaction with tungsten.
22	
23	Fig. 5 XRD results of W-Cu composites after carburization at 1100 °C in different positions of the
24	sample (a) surface layer, (b) sub-layer, and (c) substrate material.
25	
26	In order to further understand the effects of carburizing, micro-hardness, bending

1	strength and electrical conductivity were measured on the samples before and after
2	carburization, and the results are summarized in Table 2. The micro-hardness of the
3	surface layer after carburization is approximately twice that of the surface before
4	carburization, mainly due to the formation of hard carbides and carbon diffused layer.
5	On the contrary, the electrical conductivity of the W-Cu composites was decreased from
6	about 34 IACS% to 32.2 IACS% after carburization, due to the formation of WC and
7	W ₂ C after carburization. The bending strength of W-Cu composites was increased from
8	a value of 890 MPa before carburization to a value of 1104 MPa after carburization.
9	The main reason is that the maximum stress was subjected to the surface of the samples,
10	and the surface strength of the WCu composites was enhanced after carburizing. Also,
11	the tensile properties change of W-Cu composites after carburization for 30 h at the
12	temperature of 1100 °C are shown in Fig. 6. It can be seen that the engineering stress-
13	strain curves in Fig. 6 shows a similar trend (i.e. first elastic deformation, followed by
14	plastic deformation until final fracture of the samples). However, the carburized W-Cu
15	composites exhibit higher[53] yield (YS) and ultimate tensile strength (UTS) rather than
16	the uncarburized composite, i.e. the YS and UTS of carburized W-Cu composites are
17	204 MPa and 359 MPa, respectively, which are about 23.9% and 27.5% lower than the
18	original composites. These decreases in strength are mainly because the carburized
19	layer with the surface loose layer and the copper evaporation on the surface of the W-
20	Cu composites, as well as the information of the WC and W ₂ C hard and brittle phases.
21	The decreased tensile strength of the carburized WCu composites are attributed to that
22	the tensile stress is basically uniform along the cross-section of the sample, and the

surface carburized layer has a high strength and low plasticity, which contributes little 1 to the tensile stress. 2 3 Table 2 Properties of W-Cu composite before and after carburization at 1100 °C. 4 Fig. 6 The tensile stress – strain of W-Cu composites before and after carburization for 30h at the 5 temperature of 1100 °C. 6 7 Figs. 7(a) and (a1) show the SEM fracture images of original W-Cu composites. 8 9 W particles in composite mainly have demonstrated inter-granular brittle fracture, as observed in Fig. 7(a1). Also, each of the W fractures generates one large dimple and 10 11 because of the extensive stretching of this surface it appears quite featureless, because the porosity sites and solid-solid contacts are the weak point of W-Cu compacts. Thus, 12 13 the failure of composite with high content of W starts by separation of W/W and 14 develops by producing cleaved W grain after strain hardening the Cu phase and then 15 matrix rupture occurs during the tensile process. Also, the fracture morphologies of the surface region and center of the W-Cu composites after carburization at 1100 °C are 16 exhibited in Figs. 7(b, b₁) and 7(c, c₁), respectively. The dark and bright areas are W 17 and Cu phases, respectively. It can be seen that there are a lot of dimples on the fractured 18 19 carburizing surfaces (as indicated by the blue arrow). This is attributed to the surface hardening layer with a large stress owing to the different coefficient of linear expansion 20 21 of matrix (W and Cu phase) and surface layer materials (C and carbides), which results

in the generation of micro-pores due to the differences in the material properties. These pores are then grown and connected along the hardening layer and matrix as well as the boundaries of the W grains. However, from Figs. 7(c) and 7(c1), no obvious cracks are observed in the matrix of the material. The fracture process has the following sequences: (1) the separation of W-W interface; (2) the separation of W-Cu interface;
(3) the ductile fracture of Cu under the action of stress. Therefore, the key fracture
mechanism of the carburized components is a combination of brittle fracture of
carbonized layer and cleavage fracture of the substrate. This is consistent with what
have been reported in the literature for the fracture characteristics of the W-Cu
composites prepared at high temperatures and high pressures [24].

7

Fig. 7 Fracture morphology of the W-Cu composites before and after carburization at 1100°C
with a dwell time of 30h: (a, a₁) Un-carburized W-Cu composites, (b, b₁) surface and (c, c₁) matrix
of carburized W-Cu composites.

11

Based on the above results, the carburizing reaction process and schematic of the 12 W-Cu composites is proposed in Fig. 8. The W-Cu composites are firstly surrounded 13 by graphite flakes, as shown in Fig. 8(a). Because the diameter of the carbon atoms is 14 15 0.154 nm, and that of the tungsten atoms is 0.274 nm [25], therefore, C atoms easily diffuse into the interstitial octahedral spaces of the W structures at high temperatures 16 17 [26]. The carbon atoms continue to diffuse into the W structures, and simultaneously tungsten can also diffuse and migrate into the W-Cu composites due to the formed liquid 18 19 copper at the surface (as explained above). It is well-known that the carburization rates are controlled by two diffusion mechanism include mass transfer coefficients at the W-20 Cu surface and carbon atom diffusion in the W-Cu material. In the case of diffusion of 21 C into the W-Cu substrate, since activation energy for grain boundary diffusion is 22 always less than the activation energy for lattice diffusion, diffusion rate of C atoms 23 through W-W grain boundaries is always higher (Fig. 8(b)). Subsequently, the C atoms 24

1	initiate to diffuse into W grains as schematically illustrated in Fig. 8(c). This leads to
2	the formation of high C concentrations in the near surface region. As the concentration
3	of C exceeds from solubility limit of C in W, the deposition of C in W will result in the
4	formation of tungsten carbides, such as WC and W2C, especially at grain boundaries as
5	shown in Fig. 8(d). Finally, the near surface region of carburized W-Cu consists of three
6	different parts including loss layer, intermediate layer and remained matrix.
7 8 9	Fig. 8 The schematic diagram of W-Cu composite carburization process
10	Carburization process occurs along the cross-section of the sample, and is driven
11	by the carbon concentration gradient [27]. It is well known that the carburizing process
12	is strongly influenced by the carburizing temperature and time, and the rate of
13	carburization is controlled by the initial carbon concentration. Based on the well-known
14	solution of the diffusion equation for a semi-infinite body, with a constant concentration
15	of carbon on the surface, as well as the value of diffusion coefficient (Eq. (2)) [29], the
16	diffusion concentrations of carbon (C_x) can be solved using the Gauss error function in
17	the Fick's Second Law, i.e. (Eq. (3)).[28]:

18
$$D = 8.91 \times 10^{-7} \exp(-\frac{224 \times 10^3}{8.314T})$$
 (2)

The diffusion concentrations of carbon (C_x) can be solved using the Gauss error
function in the Fick's Second Law, i.e.,

21
$$\frac{C_s - C_x}{C_s - C_0} = erf(\frac{x}{2\sqrt{Dt}})$$
 (3)

where *t* is the time of diffusion, i.e. the carburization dwelling time (hr), *x* the distance from the diffuser to the interface (mm), C_s is the initial carbon concentration, C_0 is

1 the carbon concentration at a distance from the surface.

2 Following two equations present the chemical reactions between W particle and3 carbon.

$$4 \qquad \qquad 2W+C \rightarrow W_2C \qquad (4)$$

 $W_2C+C\rightarrow 2WC$

According to the W-C phase diagram [29], the above reactions (4) and (5) occur when the carbon content is over 6.0 wt.% and the temperature is larger than 1000°C. In this study, the W-Cu composites have ~80 wt.% of tungsten content (W%=80 wt.%), and the carbon content from the phase diagram at this W concentration of 80% is 4.0 wt.% (i.e., C%=4.0%). The initial carbon concentration C₀ at the surface can be set as 8.0 wt.% (see Fig. 3(b)) when the time is equal to zero. Simultaneously, it is assumed that the carbon concentration at a distance from the surface is zero.

Based on the Fick's 2nd Law and parameters we used, the distributions of carbon concentration were obtained and the results are shown in Fig. 9. The results indicate that the carbon concentration gradient decreases rapidly in the surface layer of the composites, and then tends to become steady when the carburizing temperature and time are increased. Fig. 9 also shows the measured carbon concentrations along the thickness of the cross-section of samples obtained from the EPMA results. Clearly, there is a good agreement with the experimental results and calculated ones.

20

5

Fig. 9 Results of carbon concentration distribution of W-Cu composites after carburization at 1100
 oC, obtained from analysis based on Fick's 2nd Law and experimental measurement.

(5)

1

Fig. 10 presents the friction coefficients of the carburized W-Cu composites tested at 900 °C under different applied loads measured as a function of sliding time. In generally, the friction process curve and can be divided into several points, and take the average value of the friction coefficient of all points can be considered as the average friction coefficient. The average friction coefficient can be obtained from following equation:

$$\overline{\mu} = \frac{1}{S} \sum \mu_i \Delta S_i \tag{6}$$

9 in which μ_i is the Instantaneous friction coefficient, ΔS_i Incremental braking distance 10 (m), S is braking distance (m).

It can be seen that the test had a point contact with a small amount of area contact, 11 12 and friction coefficient was not a fixed value and varied at the beginning of the friction test. However, the coefficients maintain a stable value with an increasing of the sliding 13 time. At a low contact load, the friction pair initially did not fully contact with samples, 14 thus there was more variance in the friction values. With the increase of load, the 15 fluctuation of the friction coefficient was decreased and the average friction coefficient 16 values were reduced. At a larger load, it was much quicker to change into a stable wear 17 stage. With the increase of real contact area, the pressure on unit area was smaller than 18 that of the initially contacted one, thus plastic deformation and shear friction were all 19 20 decreased. The average friction coefficient values of the carburized W-Cu composites 21 are 0.53 and 0.46 under two different applied loads (5N and 20N), respectively. To be compared with, as shown in Figs. 10(a) and (c), the average friction coefficient values 22 16

1	of the untreated W-Cu composites are 0.62 and 0.52 under different applied loads (5 N
2	and 20 N), respectively. Also, the wear rate of carburized W-Cu composite is 0.086
3	mg/h after the high temperature wear under a 5N applied load, which is much lower
4	than that of un-carburized composites (0.122 mg/h). As shown in Fig. 10 curves (b) and
5	(d), the friction coefficient of the carburized layer is relatively smaller under the high
6	temperature. The hardness value of the surface carburized layer is much higher than
7	that of the un-carburized composites (see Table 2). Also it is well-known that the carbon
8	(graphite) has a good self-lubricating effect, thus the friction coefficient can be further
9	reduced during tests.
10	
11	Fig. 10 Friction coefficient curve of W-Cu composite after carbonization at 1100 $^{\circ}$ C under
12	different applied loads measured and sliding time.
13	
14	In order to further investigate the phase composition changing of the W-Cu
15	composites after high temperature. XRD was performed on the surface of samples
16	which are subjected to high temperature wear test, and results are shown in Fig. 11. It
17	is revealed that the W and Cu phases on the surface of W-Cu composites were oxidized
18	into oxides such as WO ₃ and CuO. The oxides could temporarily protect the W-Cu
19	substrate because they possess high melting point and high hardness. Furthermore, a
20	phase of CuWO4 with brown or yellow color could be formed when the W-Cu
21	composites were subjected to a high-temperature process for a long time [30]. Erdemin
าา	[30] reported that the oxides with high ionic potentials showed low shear strength and

1	good lubricity based on the crystal-chemical model. They pointed out that (1) these
2	oxides exhibit large differences in the ionic potential; and (2) they are more stable thus
3	may lead to lower attraction between sliding surfaces. This could result in much less
4	adhesive forces across the sliding contact interfaces, hence producing the lower friction.
5	In this work, the differences of ionic potential (IP) values of tungsten oxide and copper
6	oxide are quite high (i.e., IP _{WO3} =8.8 and IP _{CuO} =5.6). Based on Erdemir's theory [28],
7	the tungsten-copper oxides of CuWO4 possess a low shear strength, therefore, the
8	friction will be reduced accordingly.

9

10 Fig. 11 The surface XRD pattern of the carburized W-Cu composites after high temperature wear.

11

12 In order to investigate the influence of oxygen content on the wear behavior of composite at high temperature, the percentage of oxygen at different wear depths of 13 W80-Cu20 composites after wear experiment at 900 °C for 40 min are shown in Fig. 14 12, along with the SEM images. The morphologies of Cu and W phases are not clearly 15 observed except that many pits and corrosion products are formed on the uneven worn 16 17 surface. Also, the oxygen content is the highest on the surface of W80Cu20 composites as shown in Fig. 12(a). With the increase of distance from the exposure surface, the 18 oxygen content decreases gradually. Furthermore, the surface pits in Fig. 12(b) are 19 much shallower than those shown in Fig. 12(a), as a result, partial exposed W particles 20 and grinding traces can be observed in Fig. 12(b). In Fig. 12(c), the morphology is the 21 same as those shown in Fig. 12(a), which indicates that the influence of oxygen content 22

1 is limited to the distance within 3 mm from the friction surface in wear condition.

2

3

Fig. 12 The content of oxygen and SEM images of W-Cu composite wear at 900 $^{\rm o}{\rm C}.$

4 4. Conclusion	
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5 (1) The carburized layer of W-Cu composites is composed of loose surface carbide
6 layer, dense intermediate layer and substrate. Phases of the surface carburized layer
7 include C, WC and W₂C.

8 (2) The micro-hardness of the surface layer after carburization is approximately 9 twice that of the surface before carburization, mainly due to the formation of hard 10 carbides and carbon diffused layer. The conductivity of the composites was decreased 11 from about 34 IACS% to 32.2 IACS%.

12 (3) The bending strength of composites was increased from a value of 890 MPa to a value of 1104 MPa after carburization. YS and UTS of carburized W-Cu composites 13 14 are 204 MPa and 359 MPa, respectively, which are about 23.9 % and 27.5 % lower than 15 the original composites due to the carburized layer with the surface loose layer and the copper evaporation on the surface of the W-Cu composites, as well as the information 16 of the WC and W₂C hard and brittle phases. Formation of oxide of CuWO₄ during high 17 18 temperature wear is beneficial to reduce friction and wear. Average coefficients of friction for W-Cu composites carburized at 900 °C under the normal loads of 5 N and 19 20 N are 0.53 and 0.46, respectively. 20

21

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7	
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Fig. 3 SEM surface morphologies and EDS results of W-Cu composites (a, a1, a2, a3) before

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