SURFACE HARDENING OF TUNGSTEN-BASED HEAVY ALLOY VIA PACK BORONIZING

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Abstract: The boronizing of a tungsten heavy alloy containing Ni and Fe as the major alloying elements were performed in the present study to increase its surface hardening. Pack cementation method was employed as a well-known, successful solid-state process for boronizing. The coating treatment was accomplished at different temperatures of 1000, 1050 and 1100°C for 6 and 9 hours. The formation of tungsten boride phase was confirmed, although a silicide layer covered the surface of the specimen as the outer layer. The mechanism of the formation of a multilayered surface was explained. The maximum thickness of reaction zone and surface hardness achieved in the current work were 300 μm and 2470 HV, respectively.

Keywords: Tungsten alloy, Hardening, Boronizing, Pack cementation.

1. INTRODUCTION

Due to the significant developments of industries and need for materials of superior quality, ceramic materials have attracted more attention. Although ceramics possess desired features like good thermal stability, high hardness, excellent corrosion resistance and high stiffness, these materials suffer from the disadvantages of high cost of raw materials, low ductility and susceptibility to brittle fracture [1]. Therefore, surface engineering has been considered for a long time to use the benefits of ceramics as the coating layers on the metallic substrates to improve their oxidation, wear, fatigue, and hardness properties [2].

Boronizing is a well-known thermochemical surface treatment that is applicable for surface hardening of a wide range of ferrous and nonferrous metals. In this process, boron atoms are introduced into the metal lattice at the surface of a work-piece to react with substrate atoms, forming a boride phase. This inward movement of the boron atoms takes place through the high temperature diffusion mechanism. Boronizing can be performed in gas state, liquid state and solid state. Because of the problems of toxic nature and expensiveness of initial materials in gaseous boronizing and technical problems in liquid boronizing, solid boronizing is normally selected in practical treatments [3, 4].

Pack cementation as the solid boronizing process can be used even for irregular surfaces of the pieces or inside the holes. This process involves burying a well-cleaned metallic substrate in a boron-containing solid powder pack and heating it to between 700 to 1100°C for 1 to 12 hours [5]. Formation of surface boride phase onto the substrate results in a substantial increase in hardness, wear resistance, corrosion resistance, and serviceability of the parts.

Literature survey shows numerous research works on the boronizing of the ferrous materials including various types of steels and cast irons to improve their surface properties [6–11]. Some of intermetallic compounds or cermet materials have also been reported to be covered by boronizing method [12–14]. There is a few works on the boronizing of nonferrous metals. The boride phases of transition metals (like WB, VB, ZrB2, CrB, NbB2, etc) are very hard and can be excellent resistive films against wear and corrosion for their weak substrates of transition metals. Usta et al. [2, 15] studied the boronizing of pure tungsten, niobium and chromium at 940°C for 2–8 hours with a constant pack composition and compared their surface characterizations. Taracki et al. [16] boronized
pure vanadium at 1100°C for 4-16 hours under
the argon atmosphere. Boronizing powder pack
used by them had a chemical composition of 90%
SiC, 5% B2C and 5% KBF4. Boronizing of
titanium alloys and the effect of rare earth
additions on the process results were also
performed [17, 18].

Tungsten is one of the hardest metals in the
periodic table. Tungsten has few, if any,
substitutes available in its key applications due to
its unique properties of heat resistance and wear
rate. Hence, tungsten is frequently identified as a
critical and strategic material. However, tungsten
is often employed as tungsten heavy alloys
instead of pure metal. Heavy metal alloys are
combinations of tungsten with nickel-iron or
nickel-copper alloying components. They are
usually produced through powder metallurgy and
sintering processes. These heavy alloys with a
boronized layer will find broader tribological
applications. Therefore, the present work focused
on the boronizing of a tungsten-based heavy alloy
by pack cementation, which has not been
reported so far.

2. EXPERIMENTAL

A tungsten heavy alloy with a chemical
composition of ~92wt.% W, ~5 wt.% Ni and
~3wt.% Fe was used as the initial substrate. The
specimens for boronizing treatment were
prepared by wire cutting in a cylindrical shape
with diameter of 7 mm and height of 5 mm. The
specimens were ground using 180-2500 grit
emery paper, polished by 0.3 µm Al2O3 particles,
and cleaned by acetone in an ultrasonic cleaner
for 10 min. Boronizing process was performed in
a tube furnace under an argon atmosphere of
99.99% purity at different temperatures of 1000,
1050 and 1100°C for durations of 6 and 9 hours
by pack cementation method. The powder pack
had a chemical composition of 90wt.% SiC,
5wt.% B2C (99%, Sigma-Aldrich), and 5wt.%
KBF4 (99%, JamPack Enterprise Ltd). This
composition for powder pack is a typical one for
surface boronizing [2, 15, 16]. This mixture was
sufficiently blended before treatment to make a
homogeneous combination. The powder pack
was enclosed by a completely sealed vessel and
subjected to the temperatures. The vessel
dimensions were 3cm×4.5cm×7cm.

The boronized samples were cleaned to
remove physically bonded powder. X-ray
diffraction (XRD) analysis were carried out on
the surface of the samples to identify the phases
formed during the treatment. A JEOL JDX-8030
instrument with Cu-Kα radiation was used for
XRD analysis. The specimens were then cut along
their diameter to study cross-sectional surfaces.
The cut samples were mounted into epoxy resin
for better microscopic observations. Microstructures were investigated by Zeiss
optical microscope and Tescan Vega II XMU
scanning electron microscope (SEM), equipped
by Rontec energy dispersive X-ray spectroscopy
(EDS) system. Vickers microhardness
measurements were carried out on the surfaces of
the specimens by a Leitz microhardness tester
under a load of 300 g for 10 s.

3. RESULTS AND DISCUSSION

3.1. Characterization

Fig. 1 (a) shows spheroidized microstructure
of the base alloy before heat treatment obtained
by an optical microscope. Spherical grains are
pure tungsten, which are surrounded by a softer,
Ni-Fe binder phase containing some dissolved
tungsten. This is typical structure of this alloy
after liquid phase sintering (LPS), which can
provide high mechanical properties. Fig 1 (b)
also shows the XRD patterns of the substrate
material before surface treatment. As seen, the
major phase is the bcc pure tungsten phase
(ICCD PDF #004-0806), and a minor phase of
Ni-Fe-W solid solution with fcc crystal structure
is observed. In this solid solution, Ni (ICCD PDF
#004-0850) is the matrix which Fe and W are
introduced within its lattice.

After boronizing treatment, XRD analyses
were performed on the surfaces of the specimens
boronized at different temperatures and times.
Figures 2-4 show the XRD results of boronizing
at 1000, 1050 and 1100 °C, respectively, for 6
and 9 hours. All XRD patterns are almost
identical and show a silicide phase as a major
surface product. At more extreme conditions of
Fig. 1. (a) Optical microstructure and (b) XRD pattern of initial tungsten based heavy alloy.

treatment ($1050^\circ\text{C}$-9h, $1100^\circ\text{C}$-6 and 9h), the major silicide phase is Ni$_5$Si$_3$ (ICCD PDF #003-1073), while at less extreme conditions ($1000^\circ\text{C}$-6 and 9h, $1050^\circ\text{C}$-6h), Ni$_5$Si (ICCD PDF #073-2029) is the major silicide phase. A small amount of tungsten boride, WB (ICCD PDF #035-0738), can also be detected along with silicide phases. Nickel, which is present in the binder areas, reacts to form surface silicide compound. The formation of different types silicide phase as a separate layer on the boride layer was also reported for boronizing of pure nickel [19, 20]. Briefly, the presence of SiC as filler material in powder pack gives rise to the formation of
Fig. 2. XRD pattern of the sample boronized at 1000 °C for (a) 6 and (b) 9 hours.

Fig. 3. XRD pattern of the sample boronized at 1050 °C for (a) 6 and (b) 9 hours.
silicide phase on the surface of specimens. In the following, the process mechanism will be explained in detail. The reason for smallness of WB peaks in XRD patterns is that the silicide layer is thick and prevents X-ray from penetration to the deeper layers.

After boronizing treatment, surface and cross section of the samples were examined. As a typical microstructure obtained after treatment, optical cross-sectional micrographs of the samples coated at 1100°C for 6 and 9 h are shown in Fig. 5 (a, b). Three regions can obviously be observed in the surfaces of the samples. These include: (a) outer layer which is mainly composed of silicide compounds (according to XRD patterns) (A region), (b) reaction zone (B region), and (c) non-affected base metal (C region). The thicknesses of reaction zones for different samples are shown in Fig. 6. As seen in this figure, increasing treatment temperature resulted in an increase in reaction zone depth. At any constant temperature, the thickness of reaction zone is also observed to increase by increasing the duration of boronizing process. In fact, the diffusion depth of boron increases with treatment time and temperature. The thicknesses of the reaction zones obtained from boronizing at various temperatures ranged between 115–207 μm and 150–300 μm for 6 and 9 hours of boronizing, respectively.

SEM micrographs in Fig. 7 show the microstructural evolutions within the reaction zone created after boronizing treatment at different processing times and temperatures. Similar to optical micrographs, the three-layered natures of the surfaces are obviously seen for all samples. The formation of such a configuration can be explained as follows.

3.2 Governing Mechanisms

The formation of the outer silicide layer
Fig. 5. Typical optical microstructure of the sample boronized at 1050 °C for (a) 6 and (b) 9 hours.

Fig. 6. Reaction zone thickness versus boronizing temperature for different boronizing time.

together with inner boride layer can be explained here. It is believed that the mechanism of the coating formation is directly related to the diffusion phenomena occurred in the material. This system is a multi-component alloy, and is different from a simple metal treatment. In an imaginary A-B alloy, it is well-known that if adding B to A lowers the melting point of A (or the liquidus line), it will increase the chemical diffusion coefficient at any given temperature [21]. Moreover, boron and silicon as the alloying constituents have been recognized to bemepting point depressing elements in high-temperature conditions [22]. Boron and silicon can be introduced into the surface as nascent atoms or gaseous species which is explained later. Therefore, the addition of boron and silicon into the surface of the base metal by diffusion causes the reduction of nickel and iron melting point and increasing their diffusion coefficients, leading to the redistribution phenomena [23]. Hence, nickel and iron that exist in the binder phase within the
Fig. 7. SEM micrograph of the samples boronized at different conditions including (a) 1000 °C–6 h, (b) 1000 °C–9 h, (c) 1050 °C–6 h, (d) 1050 °C–9 h, (e) 1100 °C–6 h, and (f) 1100 °C–9 h. The inset labeled as C1 is the same micrograph shown in (c) in a higher magnification.

reaction xonetend to change their positions because of their diffusions. They concentrate in the top sections of the surface through an uphill diffusion as a consequence of redistribution phenomena. As a result of this migration to the top areas, silicon which has a high concentration and activity on the surface due to its presence in powder pack, reacts with nickel and iron to form silicide compounds (like Ni2Si and Ni5Si2 shown in XRD patterns) as an outer layer. No
iron silicide was detected by XRD mostly due to the small amount of iron in this alloy. The elemental mapping taken by EDAX in Fig. 8 shows the concentration of Ni and Fe on the top surface in the outer silicide layer, and the reaction zone can be seen to be almost free of these elements. The formation of outer silicide layer has also been reported by others in boronizing of pure nickel [19, 20]. As can be seen in Figs. 5 and 7, microvoids were formed inside the reaction zone due to the outward transport of Ni and Fe from the binder phase areas. Boron has also diffused downhill in an interstitial regime to react with tungsten and create tungsten boride (WB), which is also shown in XRD results. Actually, reaction zone contains spherical unreacted tungsten grains which are surrounded by shell-like features with a darker color (see Fig. 7 (c1)). These affected external shells seems to be formed due to the reaction of diffused B with W on the surface of tungsten grains. Indeed, the boride phase has formed beneath the outer silicide layer. Such a core-shell configuration in reaction zone has already been reported where carburization of tungsten heavy alloy was performed to create a tungsten carbide coating [24].

The governing chemical mechanism for the formation of boride phase can be described by a series of reactions. Nascent atomic boron must be formed and diffused inward to produce boride phase. KBF₄ cannot produce nascent boron alone and BₓC plays a major role in production of atomic boron. During high temperature process, KBF₄ decomposes into KF and gaseous BF₃. The following series of reactions may be reasonable for the mechanism [12, 14, 25, 26]:

\[
\begin{align*}
KBF_4 & \rightarrow KF + BF_3 \quad (1) \\
2BF_3 + B_4C & \rightarrow 3BF_2 + 3[B] + C \quad (2) \\
2BF_3 + SiC & \rightarrow SiB_4 + BF_3 + [B] + C \quad (3) \\
3BF_3 & \rightarrow 2BF_2 + [B] \quad (4) \\
W + [B] & \rightarrow WB 
\end{align*}
\]

Gaseous SiB₄ formed in the reaction (3) can be the active agent on the surface to react with Ni and Fe to produce silicide compounds (e.g. 2Ni +
SiF₄ (g) = Ni₃Si + 2F₂ (g). The carbon produced in reactions (2) and (3) can be consumed by the following possible reactions:

\[ \text{C} + \text{BF}_3(g) = 4\text{BF}_2(g) + \text{CF}_4(g) \]  \hspace{2cm} (6)

\[ \text{C} + \text{O}_2(g) = \text{CO} + \text{CO}_2 \]  \hspace{2cm} (7)

where the oxygen in the reaction (7) may result from argon atmosphere as a minor impurity, or from remaining air in boronizing media.

3.3. Hardness Evaluation

The Vickers microhardness of uncoated tungsten substrate was measured to be about 380 HV. The silicide phase which was formed as the outer layer, is a ceramic compound with an intermediate hardness of 800-850 HV [15, 16]. To evaluate the hardness of boride layer below the silicide layer, the surfaces of samples was carefully ground to remove the silicide layer from the top. The new surfaces of the samples were subjected to microhardness test. Fig. 9 (a) shows a typical indentation mark on a grounded surface after microhardness test. Fig 9 (b) shows variations of surface hardness values for samples boronized at different temperatures and times after removing silicide layer. The dashed line in the diagram specifies the level for hardness of the substrate. The hardness of borided surfaces was greater than 2000 HV, which is typical of tungsten boride hardness [2]. The maximum hardness (2470 HV) was achieved by the sample coated at 1100°C for 9 hours. The tremendous difference between the hardness of bare and boronized tungsten heavy alloy is an obvious indication for the formation of boride phase on the surface (below the silicide layer). A slight decrease in the hardness of the samples coated at 1050°C may be attributed to the human error resulted from inaccurate grounding the surface to remove the silicide layer. As can be seen, the hardness of the samples increased by increasing the time of boronizing process. This is in agreement with the result that the thickness of reaction zone was shown to increase with increasing treatment time (Fig. 6).

4. CONCLUSIONS

A simple and effective boronizing process was successfully carried out to create a very hard surface on the tungsten-based heavy alloy. Pack cementation containing SiC (90 wt.%), B₄C (5 wt.%) and KBF₄ (5 wt.%) was used. By boronizing at temperatures of 1000, 1050, and 1100 °C for 6 and 9 hours, three distinct regions were identified on the surface of specimens. These include (i) outer silicide layer, (ii) reaction

![Fig. 9. The microhardness test was accomplished after removing outer silicide layer. (a) Typical indentation mark created after hardness test on the surface. (b) The surface hardness of the samples boronized at different temperatures for different times.](image)
zone, and (iii) base metal. Reaction zone is composed of tungsten grains with a shell of WB phase resulted from downhill diffusion of boron within tungsten lattice. The outer silicide layer creates through a reaction between outwardly diffused nickel with silicon originated from silicon-rich powder pack. The thickness of reaction zone in different samples ranges between 115–300 μm, which increases by increasing boronizing time and temperature. To reach the very hard boride layer, silicide layer was readily grounded. The microhardness of tungsten alloy substrate was approximately 380 HV, which significantly increased to about 2000–2500 HV for various boronizing times and temperatures.

REFERENCES


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