

Performance of Tungsten Alloy Hardened by Electrosark

Jia-Hui QU^a, Yan LI^{b,*}, Ce-An GUO, Yuan-Chao WANG and Hai-Long LIU

College of Equipment Engineering, Shenyang Ligong University, Shenyang, 110159, China

^aqjh915@163.com, ^bly.liyan@126.com

*Corresponding author

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Abstract. The microstructure, hardness and corrosion resistance of the tungsten alloy hardened layer, which was hardened by different power of electrosark, were investigated. The results show that the matrix and the electrode of the tungsten alloy were melted into each other after hardened by electrosark. The hardness and corrosion resistance of the hardened layer were significantly improved, and had a significant correlation with the power of the electrosark. The hardness of the hardened layer under 1600W is the largest, which improved 35.3% than the matrix. The corrosion current density of 2000W is the smallest, which is about 0.17 A/cm², and is decreased by almost two orders of magnitude than the matrix material. A dense oxide film was formed on the surface of the hardened layer in the case of the electrosark power of 2000W.

Introduction

Tungsten alloy has many excellent properties such as high density, high hardness, high melting point, high thermal conductivity, good corrosion resistance, etc [1]. In the military, tungsten alloy is often used at strong impact, high temperature, high corrosion occasions such as throat liner of solid rocket motor nozzle, inertial components, core of rod type kinetic energy projectile, etc [2]. At present, the research of tungsten alloy mainly focused on improving the mechanical properties by the addition of Co, Cr and other alloy elements [3], improving the tensile strength of tungsten alloy by microwave sintering [4], containing the growth of W grain by spark plasma sintering technology [5], producing wear-resistant and corrosion-resistant tungsten alloy material by spray deposition [6]. Magnetron sputtering, arc ion plating, laser cladding and other methods have been applied to surface hardening treatment of alloy materials [7, 8]. The microstructure, hardness and corrosion resistance are important to evaluate the performance of tungsten alloy. Research shows that the refinement of tungsten grains and solid solution strengthening can significantly improve the hardness of tungsten alloy [9, 10], the grain shape change also has an influence on the hardness [11]. In addition, the refinement of the grain and the formation of the oxide film can help to improve the corrosion resistance of the tungsten alloy [7, 12]. Research on the surface of tungsten alloy hardened by electrosark has not been reported.

The electrosark hardening is a technology which hardens the surface of the matrix by the high energy partial discharge between the matrix and the electrode, making the electrode and matrix re-alloy [13], can effectively change the material heat resistance, corrosion resistance, anti fatigue resistance and other properties, and has been widely used in the surface modification of steel and nickel based alloys. In this paper, the surface hardening of tungsten alloy by electrosark hardening technique was applied to test and analyze the microstructure, hardness and corrosion resistance of the hardened layers by different power under air condition.

Materials and Methods

W-Ni-Fe alloy, which is widely used in industry, was used as matrices and electrodes. The precursor powder was prepared by spray drying method. The precursor powder was calcinated at 650°C-750°C for 2h, reduced under hydrogen at 850°C-950°C for 2h, and pressed by cold static pressure method to obtain the rod-shaped billets with a diameter of 17mm. The Φ4mm×60mm rod

electrodes and $\Phi 15\text{mm} \times 5\text{mm}$ disc matrices were cut from the rod-shaped billets, and on stand-by after grinding, polishing and ultrasonic cleaning in acetone.

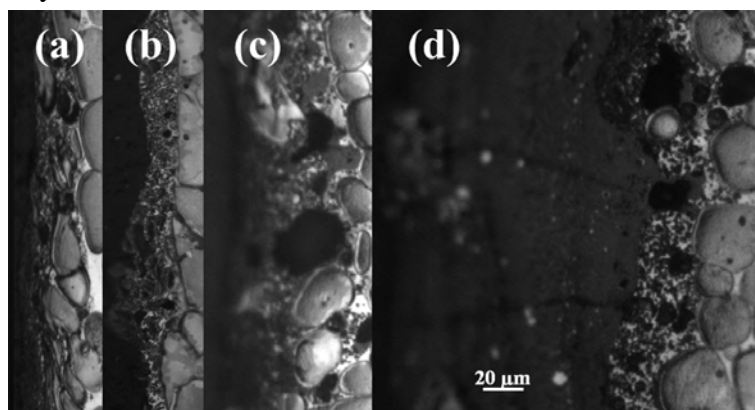
The surface of the matrices were hardened by the electrodes using the DJ-2000 adjustable power metal surface repairing machine under air condition, power of 800W, 1200W, 1600W, and 2000W, at speed of $5\text{min}/\text{cm}^2$, to get the samples with hardened layer and to compare with the matrices without hardening.

The hardened samples were packaged curing the cross section, which were corroded for 3s under the condition of 12V DC, 10% NaOH aqueous solution. An Axio Observer A1m metalloscope of ZEISS Company was used to observe the metallography. A JSM-7001F SEM with energy spectrum function was used to observe microstructure and analysis composition. The hardness of the hardened layers was measured by the nano indentation with a displacement resolution of 0.0002nm and of which can calculate the hardness by the indentation curve of the Berkovich head using the Oliver-pharr model. The corrosion resistance was measured using a P4000 electrochemical workstation, of which scanned from the corrosion potential of -200mV at speed of 0.333mV/s, fitted the measured polarization curves by the Cview software, and got the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}).

Results and Discussion

Microstructures of the Hardened Layers

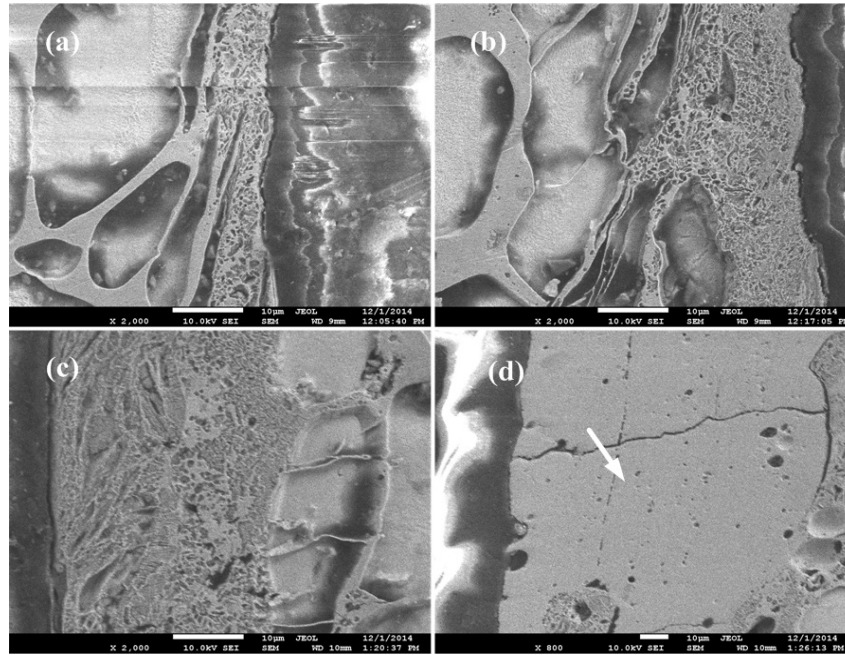
Fig. 1 show the metalloscope photographs of the sample hardened layers. The matrices and the electrodes of the tungsten alloy were melted into each other, with a thickness of $20\mu\text{m}$ under 800W and 1200W, $50\mu\text{m}$ under 1600W and 2000W. In Fig. 1(d), holes with a diameter of about $20\mu\text{m}$ are present under 2000W, and a $100\mu\text{m}$ thick dense layer distributing longitudinal cracks is present outside the hardened layer.



(a)800W; (b)1200W; (c)1600W; (d)2000W

Fig. 1 Metalloscope photographs of the hardened layers in cross-section

The SEM images of the hardened layers are shown in Fig. 2. In Fig. 2(a) and Fig.2 (b), the round grains of the transition zone between the hardened layers and matrices are stretched flat and long by the effect of the electrodes. In Fig. 2, with the increase of the hardening power, the thickness of the hardened layers is increased, and the structure is more compact. The thickness and density of the hardened layer are best under 1600W in Fig. 2(c), which shows that the matrix and the electrode are melted into each other, re-alloyed and formed the new structure instead of the original structure by the electrosparck.



(a)800W; (b)1200W; (c)1600W; (d)2000W
Fig. 2 SEM images of the hardened layers

In Fig. 2(d), the energy spectrum of the white arrow pointed is analyzed, and the results are shown in Table 1. From Table 1, it can be seen that the content of O element is high. The melting reaction of the electrode and matrix is more intense under the power of 2000W. In the high temperature environment caused by the electrospark impulsive discharge, the oxygen reaction between the molten tungsten alloy and the oxygen in the air formed a dense oxide layer outside the hardened layer.

Table 1 Energy spectrum analysis under power of 2000W

Element	Weight (%)	Atomic (%)
O	19.46	65.87
Fe	10.23	9.92
Ni	5.54	5.12
W	64.77	19.09
Totals	100.00	100.00

The thickness of the hardened layer is positively related to the electrospark power. There was a transition region formed between the matrices and the hardened layers in the process of hardening. And the shape of the grains in the transition region was changed under the action of the electrodes. With the increase of the hardening power, the outside of the hardened layer was oxidized, and a dense oxide layer was formed outside the hardened layer under the power of 2000W. Under the action of thermal stress, longitudinal micro cracks were formed in the oxide layer.

Hardness of the Hardened Layers

Table 2 shows the average hardness of the hardened layers under different electrospark power by using nano indentation. It can be seen that after the surface hardening by electrospark, the hardness of the hardened layers is obviously higher than that of the matrix, and increases with the increase of the electrospark power. The hardness under the power of 1600W is the highest, which has increased 35.3% than the matrix. It is worth noting that, under the power of 2000W, the hardness of the

hardened layer is only 3.3340GPa. The reason is that there are many holes between the grains of the hardened layer under too high power, which makes the structure relatively loose and the hardness decrease. Fig. 3 shows the hardness curves of the a-d four equal distanced measuring points from the outside of the hardened layer to the matrix under the power of 800W, which changed with the depth of the Berkovich head into the measured surface. It can be seen from the curves that the outside of the hardened layer is harder than that of the inner side, and the melting between the electrode and the matrix is more intense in the outside under the electrospark discharge. The structure of the hardened layer is more compact than the matrix. In the progress of the electrospark hardening, the electro corrosion products (gas phase, liquid phase and solid phase) of the electrodes and matrices have obvious metallurgical reaction on the matrix surface, which make the phase organization of the hardened layer different from that of the matrix. A large number of metastable ultrafine microstructures were produced in the strong temperature gradient, this kind of grain refinement and solid solution strengthening hardened the hardness of the hardened layer.

Table 2 Average hardness of the hardened layers under different power

Hardening power(W)	Average of hardness (GPa)
0(matrix)	5.160
800	6.084
1200	6.616
1600	6.982
2000	3.334

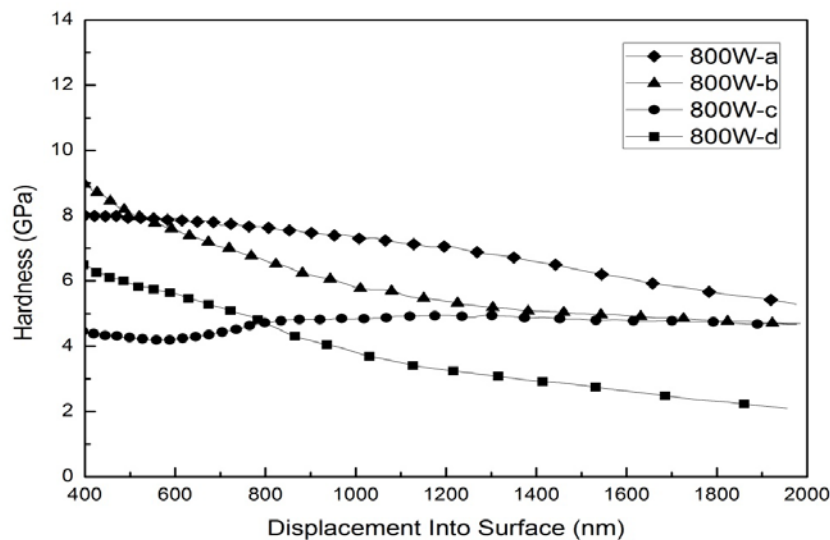


Fig. 3 Hardness of the hardened layer under power of 800W

Corrosion Resistance of the Hardened Layers

Table 3 and Fig. 4 show the results of the polarization curve fitting of the electrochemical corrosion hardened under different power. It is visible that, the minimum corrosion potential of the matrix material is about -426.5mV, the corrosion potential of the other four kinds of materials increase according to the order of 800W < 1200W < 1600W ≈ 2000W, which shows that the stronger the hardening power is, the better corrosion resistance the hardened layer has. The corrosion current density of the matrix material is the largest, about 16.3 A/cm², and the corrosion current density has the tendency of increasing first and then decreasing of the matrix and the other 4 materials. The

corrosion current density of 2000W is the smallest, which is about 0.17 A/cm², and is decreased by almost two orders of magnitude than the matrix material, indicates that the corrosion rate of the hardened layer decreases with the increase of the hardening power. Therefore, the hardened layer has a significant improvement in the corrosion resistance of the matrix, the stronger the power, the better corrosion resistance of the hardened layer.

Table 3 Fitting results of electrochemical polarization curve

Hardening power(W)	E _{corr} (mV vs SCE)	i _{corr} (μA/cm ²)
0(matrix)	-426.5	16.3
800	-350.9	0.34
1200	-344.9	4.69
1600	-279.0	2.47
2000	-283.2	0.17

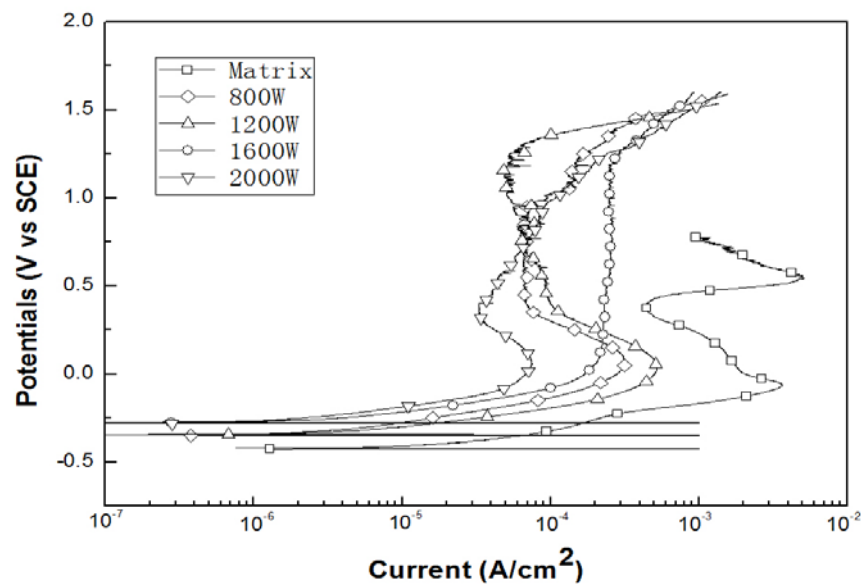


Fig. 4 Electrochemical corrosion polarization curve

Conclusions

- (1) In the process of hardening, the matrix and the electrodes are melted into each other, and the round grains of the matrix are stretched flat and long by the effect of the electrodes. The stronger the electrospark power, the thicker the hardened layer, but a dense oxide film will be formed outside of the hardened layer when the power is too strong, of which the longitudinal cracks are formed under the thermal stress effect.
- (2) The hardness of the hardened layer is obviously higher than that of the matrix, and increases with the increase of the electrospark power. The hardness of the hardened layer under 1600W is the largest, which improved 35.3% than the matrix. The hardness of the hardened layer under the 2000W power is lower than that of the matrix due to the presence of holes between grains.
- (3) The corrosion resistance of the tungsten alloy hardened by electrospark is obviously improved, and increases with the increase of the electrospark hardening power.

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