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EFFECTS OF COPPER AND HAFNIUM INFILTRATION SOURCE CATHODE DIFFERENT MIXING PROPORTION ON THE THICKNESS AND HARDNESS OF ALLOY LAYER

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ABSTRACT

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Process technique of double glow plasma chromizing was used to mutual penetration between copper and hafnium on the surface of 304 stainless steel. The surface observation and composition detection of the alloy layer were carried out by scanning electron microscopy with an of copper/hafnium infiltration on 304 stainless steel by double glow plasma technology was studied in this paper. The tec energy dispersive spectrometer. The temperature of metal was measured by ST200-Ainfrared thermometer. The hardness of sample was detected by HV1000 micro hardness tester. The results show that the different proportion of copper and hafnium has great influence on the thickness and hardness of alloying layer.

1. Introduction

Double glow plasma surface alloying technique is a kind of surface metallurgy technology based on ion nitriding. It is a new method which generates the alloy layer equipped with particular chemical qualities on common metal materials. It takes advantage of characteristics of the double glow discharge [1]. The technology creates a new field of plasma surface metallurgy [2-3]. It can generate alloy modified layer on the surface of metal material. So as to achieve the purpose of improving the surface mechanical properties and service life of the metal parts.

2. EXPERIMENTAL MATERIALS AND METHODS

The experimental matrix material is made up of 304 stainless steel, namely 06Cr19Ni10 steel. The length is 45mm, and 20 mm for width, 3 mm for height. The chemical composition of the sample is (wt%): C≤0.08 · Mn≤2.00 · P≤0.045 · S≤0.030 · Si≤1.00 · Cr: 18.0~20.0 · Ni: 8.0~11.0 and the rest is Fe. The source material is copper rod and hafnium rod which purity reaches 99.9%. The source is arranged in the barrel shaped auxiliary cathode. The size of Auxiliary cathode is 80mm for length, 120mm for width and 5mm for thickness. The structure can adjust the proportion of copper and hafnium source sputtering by regulating the number and distribution of rod source. The distance between source holes is 10 mm.

Before the experiment, the base material and the source rod were polished by different types of water abrasive paper. And then the ultrasonic cleaning machine is used to cleaning the source rod (cleaning solution acetone). Samples is hung in a auxiliary cathode as shown in Figure 1. three contrast experiments were carried out. Double glow plasma copper and hafnium experiment is conduct by LDMC-1 type multifunctional vacuum plasma heat treatment furnace.

The initial copper and hafnium infiltration process parameters on 304 Stainless Steel were as follows: gas pressure 20~30 Pa, source voltage 900V, Pole spacing 25mm, heat insulation temperature 1050° C and heat insulation time 3 h. Keeping the above experimental conditions unchanged, the quantity and source sputtering of cathode cylinder source of copper and hafnium were adjusted. The mass fraction of copper and hafnium in the source is 9:1, 4:1, 7:3, 31:19, respectively. Because the cylindrical surface area of rod like source is larger than that

of other shapes, it is helpful to increase the number of argon ion bombardment. It is beneficial to the formation of alloying layer on the surface of stainless steel.

Limited to experimental equipment function, ambient temperature is usually unstable. It will cause the copper rod to melt easily. After several tests, the copper bars in the upper and lower parts of the auxiliary cathode keep intact when the holding temperature is 1100 °C. While the copper bars in the middle part of auxiliary cathode is melted. Through the detection of infrared thermometer, the temperature of the middle part is higher than the temperature which in the upper and lower parts of auxiliary cathode. The occurrence of this phenomenon has the following factors. The sample suspended in the middle part of the auxiliary cathode is subjected to a large amount of ion bombardment during the test. So, the temperature of sample will exceed the holding temperature in the effect of ion bombardment. The diffusion effect of temperature makes the intermediate temperature higher than the other parts of auxiliary cathode. So, most part of copper rod should be inserted in the upper and lower parts of the auxiliary cathode.

After the experiment, the sample was cooled slowly to room temperature. Zeiss Axio Scope A1 Carl type optical microscope was used to observe the microstructure of the infiltrated layer. The temperature of metal was measured by ST200-A infrared thermometer. It analyzes the composition of the infiltrated layer by using Japanese JEOL/JSM-5610LV scanning electron microscope and energy dispersive spectrometer. The hardness of sample was detected by HV1000 micro hardness tester.

3. EXPERIMENTAL RESULTS AND ANALYSIS

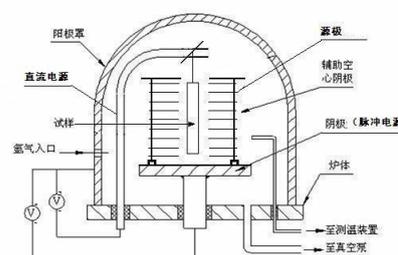
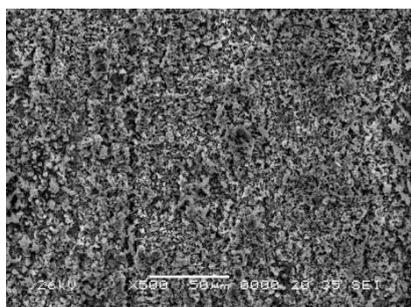


Figure 1: Schematic diagram of double glow plasma alloying equipment.**Figure 2:** Surface morphology of Cu-Hf alloying layer

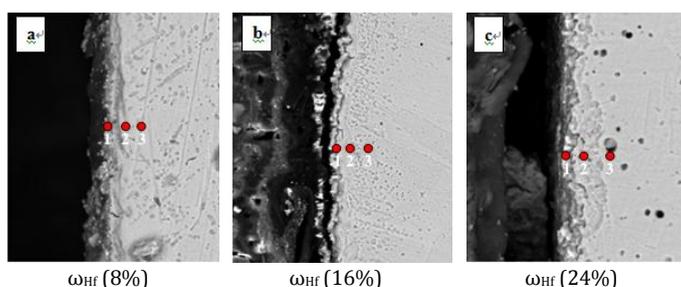
3.1 Experimental results

The experiment was carried out when the mass fraction of hafnium in the source electrode is 24%. Figure 1 shows the surface SEM morphology photograph of copper/hafnium alloying layer after finishing the experiment. The surface of copper/hafnium alloying layer has fine grain size, continuous dense distribution and no crack. The content of copper and hafnium decrease gradually from surface to interior. The main phase is Fe, Cu, Hf and Cr on the surface. Contents of Cu and Hf are 66.21%, 16.68%, respectively. It is shown that there is copper, and hafnium deposited on the surface of sample.

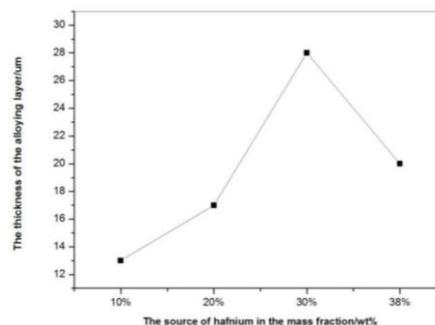
Table 1: Main components on the surface of the Cu-Hf alloying layer (mass fraction, %)

Element mass fraction/%	Fe	Cu	Hf
	7.49	66.21	16.68

Figure 3, 4 shows SEM morphology and the influence curve of the copper/hafnium alloying layer with different ratio of copper and hafnium. Table 2 is the result of the energy spectrum analysis of the points shown in Figure 3. The SEM image of the mass fraction of hafnium is showed in Figure 2. The source electrode is 8%, 16% and 24%, respectively. It can be seen from Figure 2 that the higher the mass fraction of hafnium in the source electrode, the thicker the layer will be. The thicknesses of carburized layer are 8~17 μ m, 15~22 μ m, 15~22 μ m, 20~28 μ m when the mass fraction of hafnium in the source electrode are 8%, 8%, 16%, 24%, respectively.

**Figure 3:** SEM morphology of the Cu-Hf alloying layer with different ratio of copper and hafnium

It can be seen from table 2 that the contents of copper and hafnium in stainless steel are distributed as follows: $a_1 > a_2 > a_3$, $b_1 > b_2 > b_3$, $c_1 > c_2 > c_3$, $a_1 < b_1 < c_1$, $a_2 < b_2 < c_2$, $a_3 < b_3 < c_3$. It can be seen that the hafnium element has a certain catalysis effect, but there is an optimal range of additions for the effect. As shown in Figure 3, the thickness of the layer decreases greatly when the mass fraction of hafnium in source reaches 38%. According to the principle of metals, the reason may be that the difference radius between the iron atoms and atomic of hafnium is nearly 14.4%. When the relative difference of radius between solute and solvent in the solid solution is more than 14% to 15%, it has a very limited solubility [4].

**Figure 4:** The influence curve of Cu-Hf alloying layer with different ratio of copper and hafnium

When the mass fraction of hafnium is growing, the amount of hafnium in the source increases. The solubility of hafnium in 304 stainless steel is low, and the supply of hafnium is much larger than diffusion rate of alloy elements in the work piece. Deposition layer is formed on the surface of the work piece. The bombardment of ions on the surface of the work piece is weakened, which leading the diffusion rate of alloy element to slow down [5].

At the same time, a large number of hafnium deposits on the surface of the work piece that cause the surface activity of copper reduce. Therefore, the chemical potential of the copper element in the surface is reduced, and the chemical gradient between the surface and the substrate decreases. The diffusion rate of the copper atom slowed down [6-7]. Therefore, the layer is becoming thinner.

Table 2: Composition of diffusion layer (atomic fraction, %)

No.	Distance from surface/ μ m	Fe	Cr	Cu	Hf	Ni	Mn	C	Si
a ₁	3	67.02	18.78	3.25	0.87	8.06	0.97	0.27	0.78
a ₂	14	68.81	18.24	1.43	0.28	8.71	1.14	0.03	1.36
a ₃	24	69.87	18.01	0.77	0.13	9.12	0.96	0.07	1.07
b ₁	4	64.18	19.82	4.18	1.36	8.46	0.62	0.31	1.02
b ₂	15	67.64	18.42	2.07	0.54	9.13	1.07	0.02	1.11
b ₃	26	70.14	17.31	1.21	0.16	8.97	0.95	0.11	1.15
c ₁	4	62.05	19.71	5.38	1.61	8.34	1.01	0.98	0.92
c ₂	16	67.16	18.12	3.33	0.84	8.67	1.13	0.02	0.91
c ₃	32	69.98	17.71	1.71	0.21	8.98	1.05	0.08	0.88

3.2 Mechanism analysis of thickening layer

The difference between the size of the atomic radius is relatively large. Atomic radius of hafnium is approximately 14.4% greater than that of the iron atom. The hafnium atoms dissolved in the stainless steel, which causes the distortion of the lattice of the surrounding atoms. As a result, it will have an increase in the number of vacancies and dislocations in the crystal, providing more channels for the alloying elements permeate.

Meanwhile, the diffusion activation energy decreases, which is favorable to the diffusion of copper atoms to the substrate. On the other hand, the serious distortion of the lattice is propitious to the adsorption and solid solution of copper atoms on the surface of stainless steel. Copper atoms preferentially segregate in these distorted regions. Thus, the copper concentration of layer is improved [8]. Diffusion of copper and hafnium atoms is promoted owing to the high concentration gradient of alloy surface. It improves the permeation rate and increase the thickness of the layer.

Hafnium can form oxides, nitrides and carbides directly with oxygen, nitrogen and other gases at high temperature. Therefore, it can form compounds with various elements on the surface of the work piece when it is adsorbed on the surface of steel. The surface of the work piece is purified, which is helpful to the adsorption of hafnium and copper atoms.

3.3 Hardness of surface layer copper and hafnium infiltration

As the different ratio of the mass fraction of copper and hafnium in the source shown in Table 3, the surface hardness of the hafnium-copper sample is 587HV_{0.1} (mass fraction 9:1), 605HV_{0.1} (mass fraction 4:1), 613HV_{0.1} (mass ratio 7:3), 624HV_{0.1} (mass ratio 31:19), respectively.

Table 3: Hardness of different proportions of copper and hafnium

Mass fraction ratio (Cu: Hf)	9:1	4:1	7:3	31:19
Micro hardness/HV _{0.1}	587	605	613	624

The experimental results show that the micro hardness of copper-hafnium sample is basically the same, but there is a slight difference. The reason may be that the deposition mainly consists of copper and hafnium. With the increased number of hafnium rods in the source rods, the number of sputtered hafnium is increased. It means that the number of Hafnium attached to the surface of the specimen is also increased. The copper Mohs hardness is 3, and hafnium Mohs hardness is 5.5. The deposition layer is harder that improves the measurement hardness.

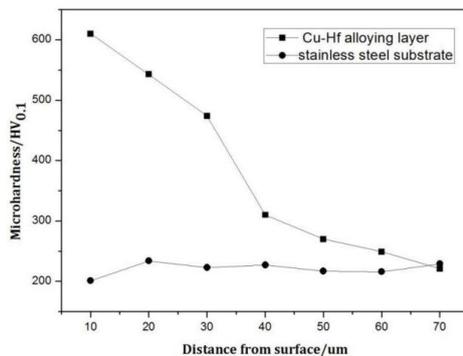


Figure 5: Section hardness curve of Cu-Hf alloying layer and Stainless-steel substrate

The Figure 5 shows that the surface hardness of the infiltrated copper-hafnium alloy layer is obviously higher than that of the 304-stainless steel substrate. There can be several reasons that the improvement of the surface hardness of the alloy layer.

Hafnium is a strong carbide forming element. After hafnium infiltrate into stainless steel substrate, it combines with carbon in stainless steel and produces a stable high hard hafnium carbide [8]. It precipitated from the solid solution and dispersed in the tissue. The hardness of the infiltrated layer is significantly improved.

The infiltration of active hafnium atoms leads to the effect of strong solid solution strengthening. Severe lattice distortion occurs in the substrate. The increase of internal energy and micro stress result in crystal slip hindered. Therefore, activation energy of grain boundary diffusion increases that hinder grain growth. The grain refinement of the alloying layer improves the surface hardness of the specimen.

4. CONCLUSION

After performing the above analyses, the following conclusions can be summarized:

(1) The surface of copper/hafnium alloying layer has fine grain size, continuous dense distribution and no crack. The ratio of copper / hafnium in the source has a significant effect on the thickness of the layer. In a certain range, the infiltration of hafnium is beneficial to the copper infiltration of 304 stainless steel. If the proportion of hafnium is more than 30%, it will hinder the growth of the layer.

(2) The performance of stainless steel matrix can be significantly improved by the infiltration of copper and hafnium. The surface hardness of the samples was higher than that of 304 stainless steel substrates. The ratio of copper / hafnium in the source rod has little effect on the surface hardness of the stainless steel. The hardness of alloy layer with copper and hafnium infiltration decrease gradually from the outside to the inside showing the gradient distribution.

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