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Surface alloying of Cu with Ti by double glow discharge process ①

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Abstract: The surface of pure copper alloyed with Ti using double glow discharge process was investigated. The morphology, structure and forming mechanism of the Cu-Ti alloying layer were analyzed. The microhardness and wear resistance of the Cu-Ti alloying layer were measured, and compared with those of pure copper. The results indicate that the surface of copper activated by Ar and Ti ions bombardment is favorable to absorption and diffusion of Ti element. In current experimental temperature, as the Ti content increases, the liquid phase occurs between the deposited layer and diffused layer, which makes the Ti ions and atoms easy to dissolve and the thickness of Cu-Ti alloying layer increase rapidly. After cooling, the structure of the alloying layer is composed of CuTi, Cu_4Ti and Cu(Ti) solid solution. The solid solution strengthening and precipitation strengthening effects of Ti result in high surface hardness and wear resistance.

Key words: titanizing; Cu-Ti alloying layer; double glow discharge process
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1 INTRODUCTION

Copper has many application in electrical, electronic and heat exchanger fields because of its superior electrical and thermal conductivity and better corrosion resistance. However, the wear resistance of copper is poor. Being both soft and ductile, surface of pure copper are easily deformed and scratched, particularly at high temperature. Copper-based alloys are developed to improve some properties of copper. For example, Cu-Ti alloys have high tensile properties and reasonable wear resistance, and are applied in relatively high wear applications such as plastic injection moulding dies where the relatively high thermal conductivity of the copper alloy when compared with, for example, tool steel, is damended. However, the thermal conductivity of the bulk Cu-Ti alloy is lower than that of pure copper[1-3].

Surface engineering, as opposed to bulk alloying, provides an opportunity to improve the wear resistance of copper and copper alloys while leaving the bulk characteristics relatively unchanged. By this method, optimizing of the properties of the surface and the bulk can be realized. However, there is limited information available on the surface engineering of copper and its alloys. The double glow plasma surface alloying technique, known as the Xu-Tec Process[4,5], is a hybrid plasma surface treatment technique which involves both plasma nitriding and sputtering techniques, and has been developed to satisfy the need for high quality alloy layer at the surface of less expensive materials. This technology employs low temperature plasma produced by the double glow discharge to drive metal atoms of one or more elements to deposit and diffuse into the substrate surface. Energetic metal atoms combine with atoms of the substrate to form an alloyed layer up to 300 μm thick. For example, nickel-chromium base alloys, high speed steels and various alloys have been formed on the surface of common carbon steels and other conductive materials[6-10]. Compared with ion implantation or laser surface alloying, this process is simple and versatile in that a large number of metals and their combinations can be diffused into the substrate.

In the current study, pure copper substrate was alloyed with Ti using the Xu-Tec Process. The distributions of Ti, hardness from surface to substrate and the wear characteristics on the surface were measured and analyzed. The formation mechanism of Cu-Ti alloying layer was discussed.

2 EXPERIMENTAL

2.1 Apparatus

The Xu-Tec Process is performed in a vacuum chamber. Fig. 1 indicates the working principle of this process. In the vacuum chamber, there are three electrodes: the anode and two negatively charged members called as the cathode(Cu sample) and source electrode(Ti sheet) respectively. Both the cathode and source electrode are surrounded by double glow discharge with two DC power supplies. One glow discharge heats the Cu substrate while the other strikes the source electrode. The Ti ions or atoms sputtered from the source electrode are accelerated toward the Cu substrate at a higher negative potential, then de-

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posit and diffuse into the copper surface forming a Cu-Ti alloy. The vacuum chamber was kept at 2 - 3 Pa, then back-filled with argon to 20 - 40 Pa before double glow discharging. The cathode(Cu sample) was heated by ion bombardment to 940 - 950 ℃ and was maintained at that temperature for several hours. The holding time depended on the thickness required and on the actual temperature. After titanizing operation was completed, let the sample cool down in the chamber under the protection of Ar. In current experiment, the source electrode potential was more negative than the cathode potential.

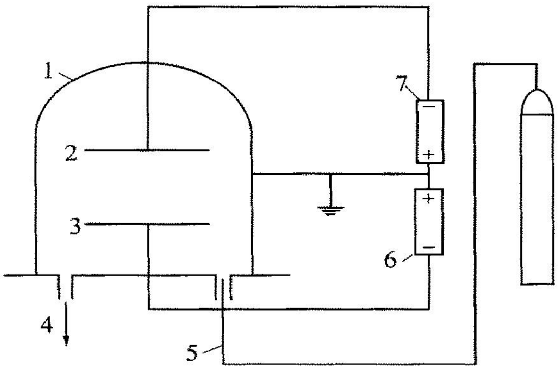

Fig. 1 Schematic diagram of experimental apparatus
1 —Shell (anode); 2 —Source electrode;
3 —Cathode (Cu sample); 4 —Vacuum pump;
5 —Inert gas inlet; 6, 7 —DC power supplies

2.2 Material and experimental conditions

Tests were performed on rectangular(50 mm × 30 mm × 3 mm) pure copper specimens (Si ≤ 0.007%; Fe ≤ 0.072%; P ≤ 0.019%; Sn ≤ 0.028%; P ≤ 0.007%; Cu ≥ 99.8%, mass fraction). Prior to testing, the specimen surface was finished to 1 200 μm with silicon carbide abrasive paper, rinsed in de-ionized water, degreased in acetone and dried in air. The source electrode(130 mm × 130 mm × 6 mm) has a chemical composition of 0.1% C, 0.3% Fe and balance Ti(mass fraction). It was immersed in the hydrofluoric acid solution (HF: HNO_3: H_2O = 1: 3: 7, volume ratio) for 5 min to remove the oxidizing film before testing.

Based on the considerable experiment, the operating parameters of Xu-Tec process in the tests are gained and listed in Table 1 together with the final thickness of Cu-Ti alloying layer.

The morphology and structure of Cu-Ti alloy layers were investigated by scanning electron microscopy (SEM). The distributions of Ti element were examined by SEM(LEO-438VP) equipped with EDS. The micro-hardness from surface to substrate and the wear resistance of the alloying layers were measured with micro-sclerometer (M400-H1) and MM200 wear tester, respectively. The surface phase structure of Cu-Ti alloy layer was measured with Rigaku D/max 2500 X-ray diffractometer.

3 RESULTS AND DISCUSSION

3.1 Microstructure and formation mechanism of Cu-Ti alloy layer

The SEM micrographs of Cu-Ti alloy layer are shown in Fig. 2. From Fig. 2(a), it can be seen that the Cu-Ti alloy layer consists of two parts: deposited layer and diffused layer and there is a boundary between them. Fig. 3 shows that Ti content decreases quickly from surface to about 20 μm deep but thereafter decreases slowly. The change of the decrease rate of Ti content suggests that there are the deposited layer and diffused layer. Fig. 2(b) shows the surface morphology of Cu-Ti alloy layer. The composition of the white particles is, measured in mass fraction, Ti: Cu= 43.54: 55.62, which is the TiCu compound according to the Cu-Ti binary phase diagram[11, 12]. This is in agreement with the result measured by Rigaku D/max 2500 X-ray diffractometer (Fig. 4). From Fig. 4, the alloy layer consists of Cu-Ti, Cu_4Ti and Cu(Ti) solid solution.

The process of surface alloying is usually considered to be controlled mainly by alloying element diffusion. There are originally three or four different models to explain the migration of these substitutional atoms, but one, the vacancy model, which can explain most availably the experimental evidence, has become increasingly popular. In the vacancy model, the diffusion coefficient is easily derived as follows[13].

Table 1 Operating parameters of Xu-Tec process

Exper. No.	Source electrode		Cathode		Distance between source electrode and cathode/mm	Ar pressure/Pa	Temperature/℃	Time/h	Thickness of Cu-Ti layer/μm
	V_s/V	I_s/A	V_c/V	I_c/A					
1	950	1.3	380	1.8	20	30 - 35	940	3	75
2	980	1.4	400	2.1	20	30 - 35	965	3	80

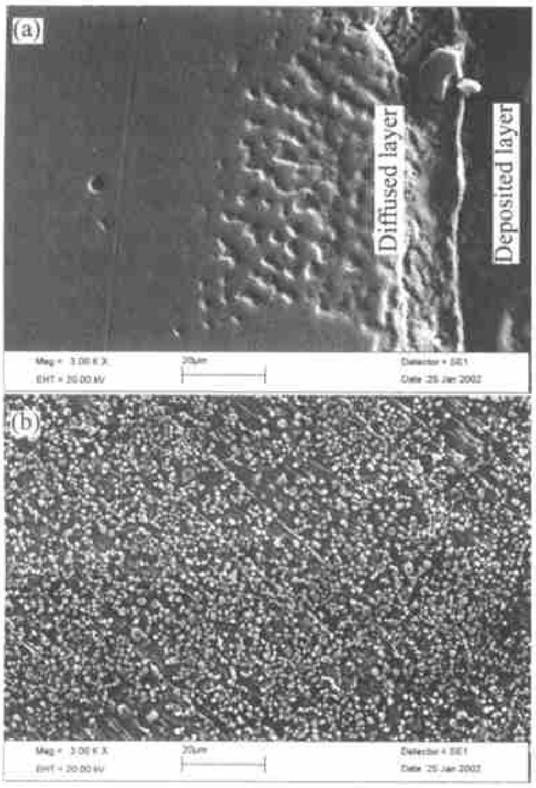

Fig. 2 SEM micrographs of Cu-Ti alloy layer
(a) —Cross section; (b) —Surface

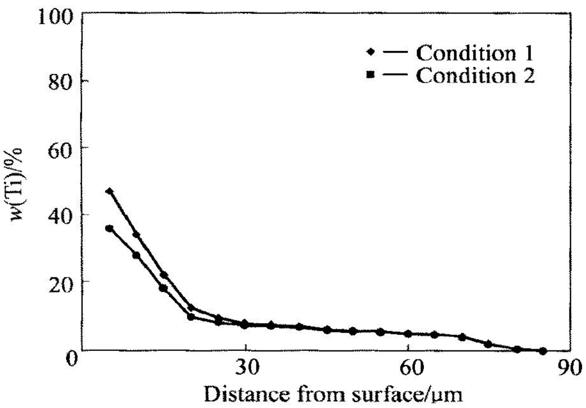

Fig. 3 Distribution of Ti content in Cu-Ti alloying layer under different process conditions

$$D = D_0\exp\left[-\frac{Q_{vf}+Q_{vm}}{RT}\right] = D_0\exp\left[-\frac{Q_{sd}}{RT}\right] \tag{1}$$

where Q_{vf} is the activation energy for vacancy formation, Q_{vm} the activation energy for vacancy migration, and Q_{sd} the activation energy for self-diffusion of solvent atoms. It should be noted that the activation energy for self-diffusion in a pure metal should be equal to the sum of the activation energies for vacancy formation and migration. The same arguments are applied for diffusion of substitutional solutes by the vacancy mechanism. In most cases, it gives an intrinsic diffusion activation energy Q_{id} similar to or a little lower than that for self-diffusion.

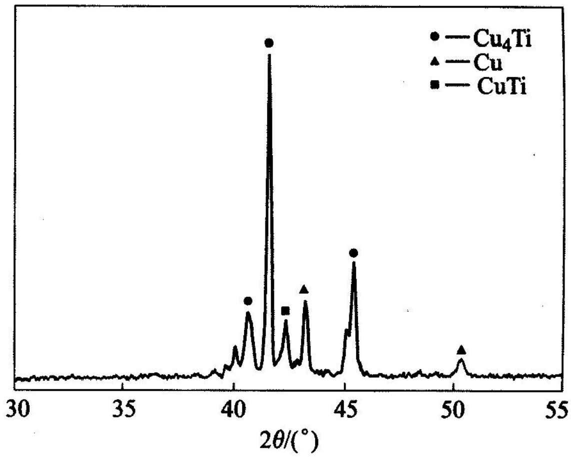

Fig. 4 XRD pattern of Cu-Ti alloying layer

In double glow discharge process, however, the collision of high enevgy ions with the surface of specimen will produce a high concentration of vacancies on the treated surface[13]. In current investigation, the Ti ions and atoms from source electrode can be free to diffuse into the Cu substrate. The solid FCC copper has a fairly large solubility of titanium. This speeds up the diffusion velocities and thickening of the diffusion layer.

With the increase of Ti content, the surface of diffused layer gets into liquid (Cu) solid solution region, according to Cu-Ti phase diagram. So Ti and Cu atoms will dissolve directly into liquid, which makes the thickness between the deposited layer and diffused layer increase quickly. Afterwards, as the Ti content increases further, the surface of diffused layer comes to the single liquid region. This makes Ti and Cu atoms easier to dissolve and diffuse, and the Ti content increases more rapidly.

During the cooling course, a series of reactions occur in the liquid:

$L \rightarrow L_1 + L_2$, $L_1 \rightarrow (Cu)$,

$L_1 + (Cu) \rightarrow TiCu_4$, $L_1 \rightarrow TiCu_4 + TiCu_2$,

$L_2 \rightarrow TiCu$, $L_2 + TiCu \rightarrow Ti_3Cu_4$,

$L_2 + Ti_3Cu_4 \rightarrow TiCu_2$, $L_2 \rightarrow TiCu_2 + TiCu_4$

Afterwards the compound $TiCu_4$ forms a eutectic together with $TiCu_2$[14]. The eutectic reaction occurs at 875 ℃ with 27% Ti(mole fraction). $TiCu_4$ may thus be formed both from liquid and from solid phase. It should be noted that $TiCu_2$ is present only at a narrow temperature range and not at room temperature. This explains why there does not exist $TiCu_2$ and Ti_3Cu_4 on the surface of alloy layer.

3.2 Properties of Cu-Ti alloy layer

The curves of microhardness distribution from surface to the Cu substrate are shown in Fig. 5. It has the same trend with Ti content distribution. This

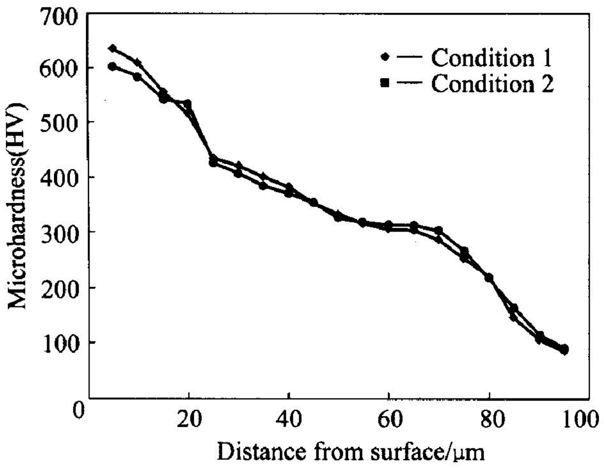

Fig. 5 Microhardness of Cu-Ti alloying layer

shows that the microhardness of alloy layer depends on the Ti content. Increasing the Ti amount of surface layer causes an increase in the peak hardness. In Fig. 6, it can be noted that the wear resistance of alloy layer is increased remarkably, compared with that of pure copper.

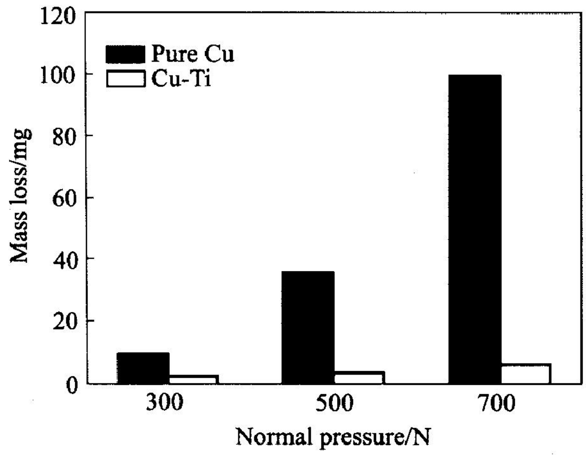

Fig. 6 Results of wear test at different normal force

4 CONCLUTIONS

Ti-alloying on the surface of pure copper is realized with double glow discharge process. The reasonable process parameters (V_s: V_c> 2, Ar pressure 25 - 40 Pa, distance between source electrode and cathode 18 - 22 mm, temperature 940 - 970 ℃) are the elementary conditions. The Cu-Ti alloying layer consists of deposited layer and diffused layer. In the first stage, due to the collision of high energy ions with the surface of specimen, a high concentration of vacancies formed on the pure Cu surface, which promote the adsorption and diffusion of Ti atoms. The increase of liquid phase speeds further up the mutual diffusion of Cu and Ti atoms. In depth direction alloying layer is followed by a gradual decrease of the Ti content. The structure of the alloying layer is composed of CuTi, Cu_4Ti and Cu(Ti) solid solution. The solid solution strengthening and precipitation strengthening effects of Ti result in high surface hardness and wear resistance.

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