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Study on Preparation and Properties of Novel Ti/Cu Laminated Composite Electrode Materials

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Abstract: *This paper starts with the structure design of the electrode base material, Ti/Cu electrode material instead of single metal Ti as the base material which was prepared by hot diffusion welding, the change of composite material structure is influences on electrochemical properties of Ti/Cu that was analyzed by SEM, electrochemical workstation and so on. The results show that the design changes of matrix structure of traditional Ti electrode is good for enhance the electrochemical performance of electrode, due to the design of layered composite structure was used, the inner Cu of composite material is current collector electrode and conductive channel carrier , it reduces the resistivity of the electrode material (its resistivity is only 1/15 of pure titanium electrode material) and improves the electrical conductivity of the electrode, in order to realize the uniformity of the current in the electrode, the electrochemical performance of the electrode was improved for the novel Ti/Cu laminated composite electrode materials.*

Keywords: Ti/Cu laminated composite materials; Hot press diffusion welding; Electrochemical performance; Surface potential distribution

1. INTRODUCTION

In modern society, non-ferrous metals is an important material base to the development of science and technology, national economy and national defense construction, it is the key strategic resource to upgrading the comprehensive national strength and ensure national security[1]. With the increasing scarcity of metal ores, the wet metallurgy process which has its unique advantages will be one of the main methods to nonferrous metal extraction, and the process of wet metallurgy requires a large amount of energy, environment and resources. However, electrode is not only an important part of equipment in that process, but also is the main body and core of the electrochemical reaction system in that, its performance will directly affect the reliability of the whole process of electrochemical reaction (including the quality of products, the stability of the operation process, energy consumption and environmental pollution). So, the electrode material is the key factor in the electrochemical reaction system[2-4].

It is mainly based on the anode of lead alloy and titanium coating anode in the process of wet extraction of nonferrous metals at present[5,6]. Titanium based coating anode has been widely used in the field of wet metallurgy extraction which has size stability, shape diversity and excellent electrochemical properties, whereas the resistivity of titanium is large, that limits further application and performance improvement[7-9].

According to the performance characteristics of metal matrix composites[10,11], Ti/Cu layered composite materials instead of

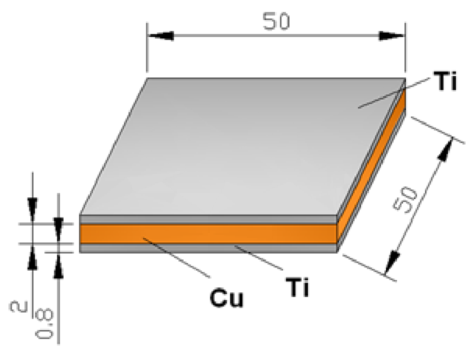

Figure 1. Sample Stacking Order and Size

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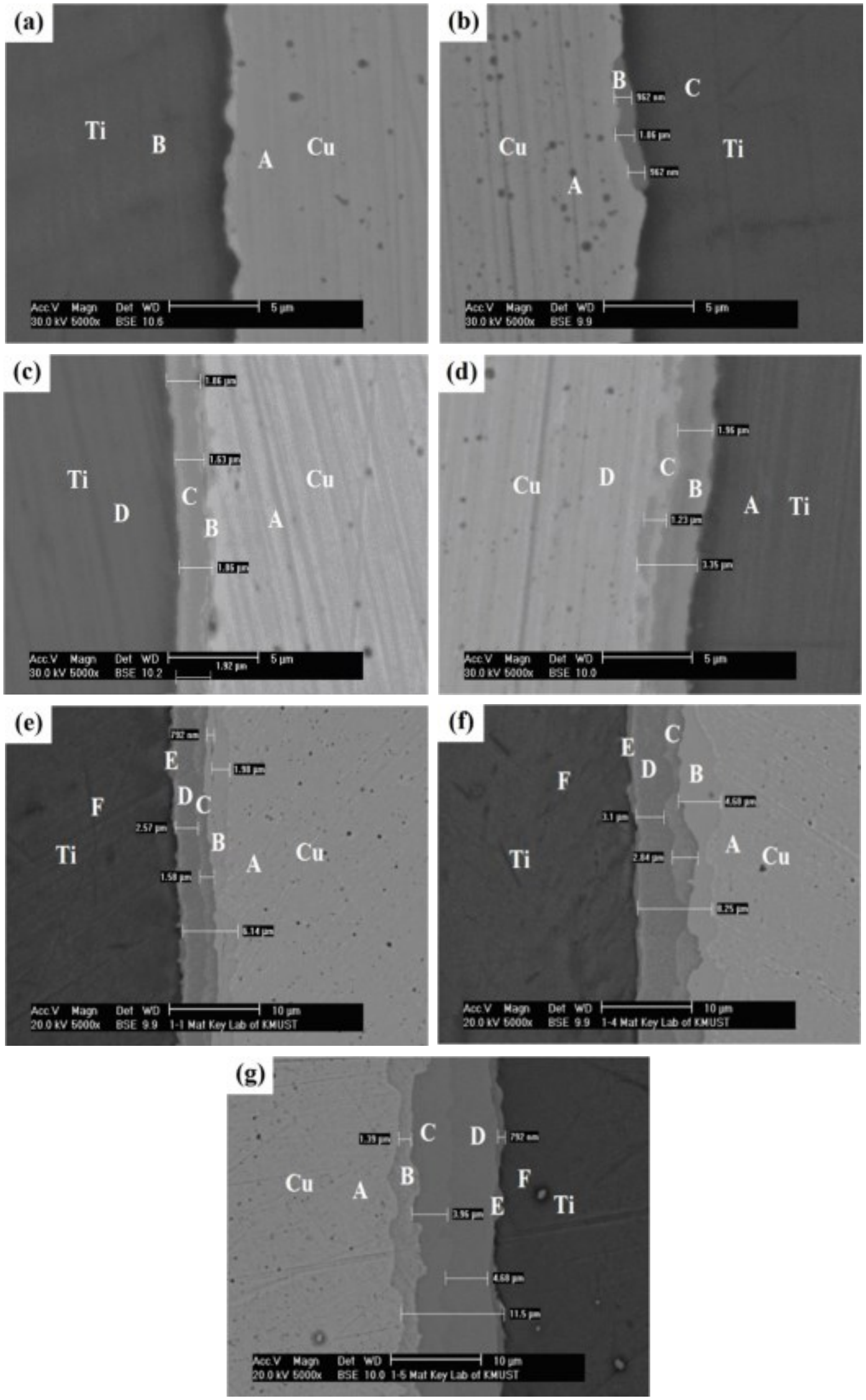

Figure 2. Microstructure Structure of Ti/Cu Welding Joints Welded at Different Temperature. (a)T=620ºC, (b)T=640ºC, (c)T=660ºC, (d)T=680ºC, (e)T=720ºC, (f)T=800ºC, (g)T=820ºC

the traditional single metal Ti as the electrode substrate, the inner core metallic Cu is collecting electrode and a conductive channel carrier which role is to reduce internal resistance, accelerate the speed of transmission, reduced electrode polarization potential and uniform the distribution of current, so as to improve the performance of electrode materials.

2. EXPERIMENTAL PROCEDURE

We use industrial pure Ti (TA1) and pure Cu boards in this study, the sizes of the samples were Ti – 0.8mm×50mm×50 mm, Cu – 2mm×50mm×50 mm. Oxide films of Ti and Cu could form easily on each surface. The surfaces of Ti and Cu had to be processed before welding or they would prevent the diffusion of Ti and Cu. The Ti surfaces were processed as follows: 10% of the alkaline solution→distilled water→5%HF+15%HNO_3→distilled water→vacuum oven dried; The Cu surfaces were processed as follows: 10% of HNO_3→distilled water→distilled water→vacuum oven dried. The diffusion welding equipment was used in the experiments. The main parameters of the equipment were as follows: the maximum vacuum degree was 1.0×10^{-3} Pa; the highest welding temperature was 1200ºC; furnace body for the protection of Ar atmosphere. The electrode material was prepared sample shown in Fig.1, The change of process parameters is shown in Table 1.

The microstructures and interface features of the Ti/Cu composite materials were observed using a Philips XL-30 ESEM scanning electron microscope (SEM). The resistivity of the Ti/Cu composite materials was measured by Four-probe method. The electrochemical performance of the Ti/Cu composite materials were analyzed using a CHI600A electrochemical analyze instrument.

3.RESULTS AND DISCUSSION

3.1. The microstructure of diffusion zone

These pictures indicate that the higher the temperature of the heat diffusion welding process, the more types of intermetallic compounds appeared, the more number of diffusion layers and thickness of each diffusion layer, the relationship between the thickness of each diffusion layer and temperature was linear. The relationship between the growth rate of diffusion layer and welding temperature was linear under the condition of lower temperature, Fig.3 is the variation of the thickness of the sample interface with the welding temperature is between 620ºC and 820ºC.

We can be seen from Fig.2 (f),the diffusion layer of the interface

Table 1. The experimental parameters of different thickness of Al and Ti

No.	Welding temperature /ºC	Holding tim/min	Static/MPa
(a)	620		
(b)	640		
(c)	660		
(d)	680	60	10
(e)	720		
(f)	800		
(g)	820		

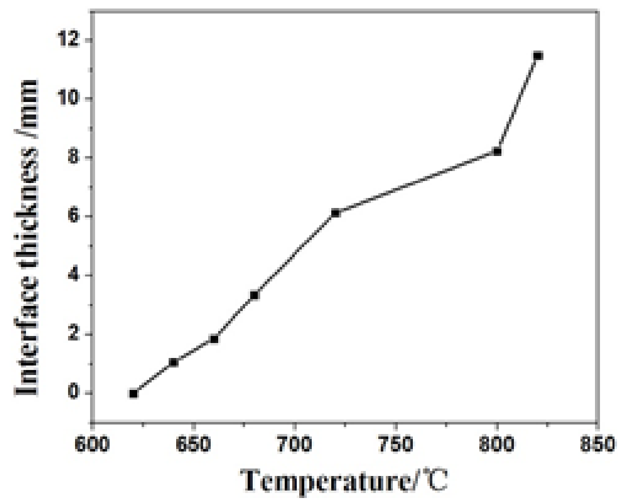

Figure 3. The Relationship between the Thickness of Diffusion Layer and Temperature

is composed of 4 sub layers, the thickness of D layer is the largest and that of C layer is smaller, although the B layer is produced earlier, but the thickness is the most thin, as well as the shape of the interface of each sub layer is not straight, but showing a wave raised to the Cu substrate. And the thickness of the diffusion layer is the most in Fig.2 (g) ,the diffusion layer of the interface is also composed of 4 sub layers, it is the same as the structure of the Fig.2(e) and (f).

Four layers of intermetallic compound layer are formed at the interface of the welding material when the temperature is above 700ºC, as shown in B, C, D, E of Fig.2(e) and (g). With the increase of the welding temperature, The thickness of each layer in the interface diffusion layer increases, the B layer increases from 1.98μm to 4.68μm, the C layer increases from 1.58μm to 3.96μm and the D layer increases from 2.51μm to 4.68μm.

Through the analysis and comparison in the picture Fig.2, we found the total thickness of the diffusion layer and the thickness of each layer are increased With the increase of welding temperature. Temperature provides energy for the diffusion of atoms in the process of diffusion welding, according to the Arrhenius equation[12], the higher the temperature of the heat diffusion welding process, the more diffusing activation energy of atoms, the migration of atoms is more likely to occur, and the more the diffusion coefficient of atoms, so the more severe degree of interface reaction to cause thickness of the diffusion layer is widened. Furthermore, only the thickness of the diffusion layer increases, and there is no increase in the number of internal sub layer when the welding temperature is increased from 720ºC to 820ºC.

Cu and Ti elements continue to spread through the contact interface both sides of the contact interface between Ti and Cu under the combined action of welding temperature, holding time, pressure and concentration gradient when they spread, there is diffusion layer that its structure is not the same as that of the matrix after the diffusion reaction between the elements. The thickness of the interfacial intermetallic compound layer is increasing with the increase of temperature. And, it can aggravate local plastic deformation to

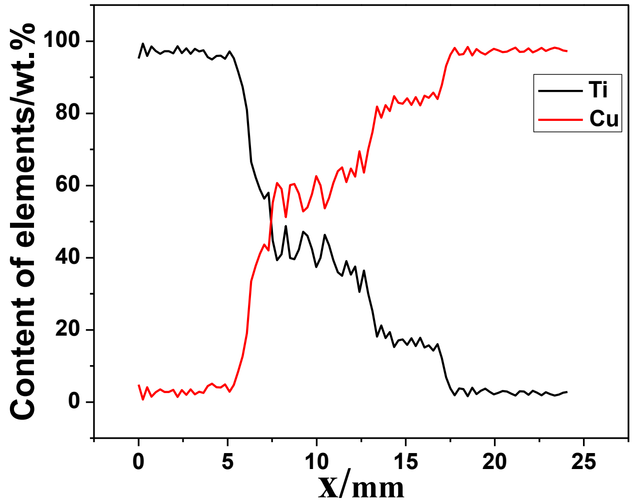

Figure 4. Ti and Cu Concentration Curves of Ti/Cu Diffusion Zone under 820ºC, 10MPa, 1h

the increase of temperature, it speeds up the atomic motion, atomic activity ability enhancement to increase the interface reaction, so that the thickness of the diffusion reaction layer is increased.

3.2. EDS analysis of the welding interface of the composite materials

A linear scan was performed in this study which is from the Ti side to the Cu side in diffusion interface of Ti/Cu, its atomic concentration is gradually decreasing with the increase of diffusion distance to Ti, the concentration changes of its show a step like pattern which is consistent with the characteristics of solid reaction diffusion, as show in Fig.4. With the diffusion reaction, the diffusion of the whole reaction are formed by the diffusion and phase transition of the Ti and Cu components. There are concentration mutations in the interface, the concentration distribution is not continuous in the interfacial diffusion zone, so there occurred heterogeneous reactions in the diffusion interface with component change.

In order to study the phase structure and composition of the diffusion reaction layer on the Ti/Cu interface, it conducts EDS point analysis in this study. We find that Ti/Cu diffusion interface has some differences in the same layer zone composition under different temperature, and it is also different to formed intermetallic compound by different process parameters, as show in Fig.5 and Table 2.

Table 2. EDS microanalysis of the reaction zone

	Location on micrographs	Elements in atom percentage(%)	
		Ti	Cu
(a)	1	99.49	0.51
	2	44.42	55.58
	3	35.98	64.02
	4	19.71	80.29
	5	16.17	83.83
	6	01.05	98.95
(b)	1	97.98	2.02
	2	64.64	39.36
	3	43.25	56.75
	4	35.68	64.14
	5	16.19	83.81
	6	0.95	99.05

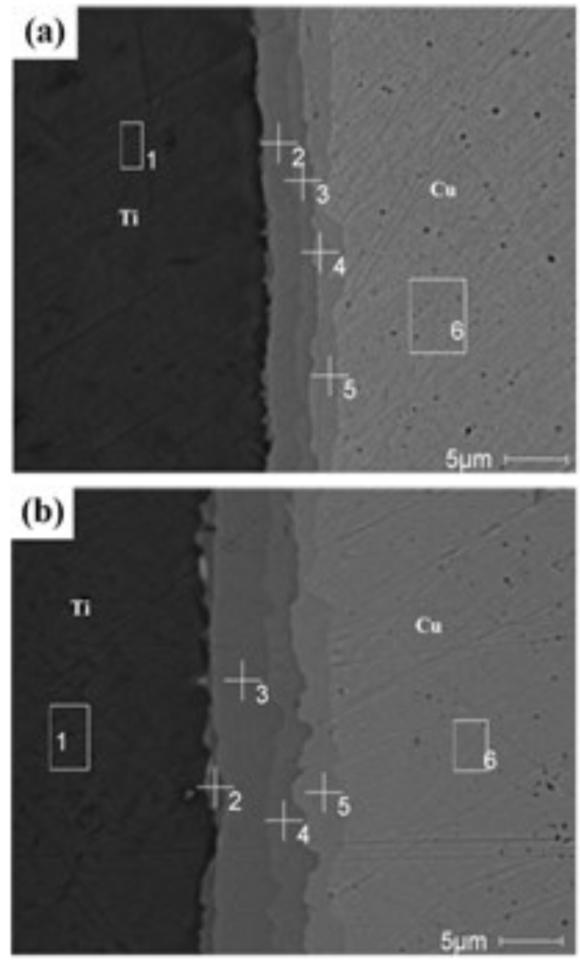

Figure 5. EDS Spectrum of Reaction Diffusion Zone (a)720ºC; (b) 820ºC

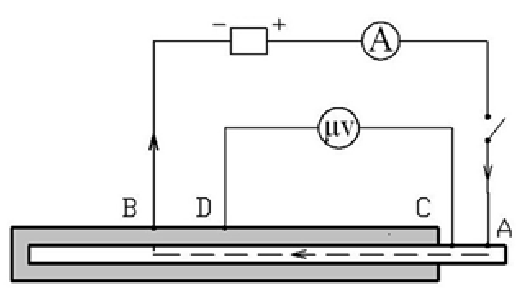

Figure 6. Diagram of Four-point Probe Resistance for Electrode Material Test

We can be seen from Fig.5 and Table 2, under the temperature is 720ºC, the metal compounds that may be formed from the Ti side to the Cu side are: CuTi, Cu_3Ti_2, Cu_3Ti and Cu_4Ti, according percent of atomic mass and EDS point analysis. And when the temperature is 820ºC, the metal compounds that may be formed from the Ti side to the Cu side are: $CuTi_2$, CuTi, Cu_3Ti_2 and Cu_4Ti, there is a new phase $CuTi_2$ in that, and Cu_3Ti phase is not generated at low temperature. So, according to the phase diagram of Ti/Cu[13], we know that Cu_3Ti encounter phase transition as the intermediate phase with the increase of temperature.

3.3. The the resistivity of the composite materials

According to Ti-Al composite electrode material the path of the electric current import and export in actual use and the principle of four-probe resistance measurement, the way of wiring shown in Fig. 6 in this study. The resistivity of sample is calculated according to Table 3.

The results from four-probe resistance measurement, Table 3 shows that the Ti/Cu composite electrode material had dropped significantly, about 1/15 resistivity of pure Ti. With the welding temperature rises, the resistivity of the sample will be reduced and then increased. Since the internal resistance of Cu is only 1 / 28 of Ti resistance, the composite material relative to the overall resistance of pure Ti decreased significantly. However, the different welding temperatures on the resistivity of composite materials are not very significant. From Cu to Ti is the shortest path about the movement of electrons, so the resistivity of composite materials decreased significantly. But the diffusion reaction layer is very small in this experiment, and its widest point is only 11μm, according to resistance formula: $R = \rho L / S$, where L is the number of class 10^{-5}, 10^{-5} that resistance is orders of magnitude, even if the resistivity of the alloyed layer increases, its seems negligible to the overall resistance of the composite material. Therefore, when the Ti/Cu composite resistance decreases the aluminum layer play an important role, the thickness of the reaction followed.

3.4. The electrochemical properties of the composite materials

Excellent electrochemical performance has a vital role to the application of electrode material. Therefore, the electrochemical properties of the composites were tested by the electrochemical analyze instrument. We tested the steady-state anodic polarization curve by the linear sweep voltammetry (LSV) in the saturated KCl solution. The results shown in Fig.7, where the $0^{\#}$ sample is pure Ti.

Ti/Cu composite electrode materials and the pure Ti electrode polarization curve similar to the chlorine evolution. When the potential is less than 1.05V, the current does not change the basic, but when the potential is greater than 1.05V, all the electrodes of the current changes are obvious with the potential rise, and the current increases much faster than pure Ti electrode current changes. So Ti/Cu composite electrode materials, is better than pure Ti anode in the polarization performance.

As described above, the diffusion welding of Ti/Cu can be summarized as follows: (1) When the temperature<620ºC, the diffusion reaction layer of Ti and Al did not appear, and their electrochemical properties is poor, just as in Fig.2 (a) and Table 3. Because the welding temperature low, Ti atoms and Al atoms do not have enough activation energy of diffusion to make the diffusion, and they are just a mechanical bond. Therefore, the electrode be able to overcome the potential barrier and cross the interface of Ti and Cu in the process of electron motion, and it suffered a larger resistance, the electron velocity is slow relatively and electrical conductivity is poor relatively, so their electrochemical properties is poor; (2) Gradually increased as the welding temperature, When the welding temperature reaches 640ºC, the diffusion reaction layer of Ti and Al appear obviously, and their electrochemical properties has been improved, Ti and Al combination to achieve the metallurgical type, just as in Fig.2 (b)-(g) and Table 3, Ti/Cu intermetallic compound is the diffusion reaction in the diffusion reaction layer. As the temperature continues to rise, the diffusion reaction of Ti and Cu can be fully, the product of the diffusion reaction increased and widening the thickness of diffusion reaction layer, as well as the product of the diffusion reaction occurs phase transition process, leading to its resistance changes in the process of electron motion, there is Cu_3Ti in the interface that the electron suffered the greater resistance and the more difficult movement of electrons than that of $CuTi_2$, the conductivity decreased with the decline in the electrochemical performance. Therefore, it affects the electrochemical performance of electrode materials both the thickness and the phase composition of the diffusion layer, the composite material can be better electrochemical performance when the diffusion reaction have the same product.

Table 3. Date of Conductive Test of Ti/Cu Samples

Samples	620ºC	720ºC	760ºC	800ºC	820ºC	Pure Ti
$\Delta\Phi$/μv	13.1	10.7	10.0	10.2	12.8	159.2
β/μΩ·m	4.7	4.2	4.3	3.2	3.5	55.6

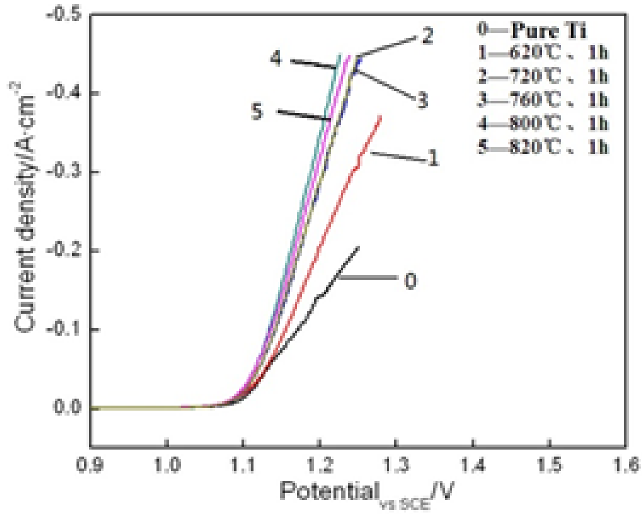

Figure 7. The polarization curve of electrode with temperatures changes to Ti/Cu composite electrode material

Table 3 shows that the welding temperature on the electrochemical properties and resistivity of the composite materials has the impact of the same law. The electrochemical catalytic activity of electrode will be increased 10 times when the electrode overpotential is decrease by 100mV[14]. According to Fig.7, Ti/Cu composite electrode material has a high electrochemical activity and the excellent electrochemical performance to pure Ti.

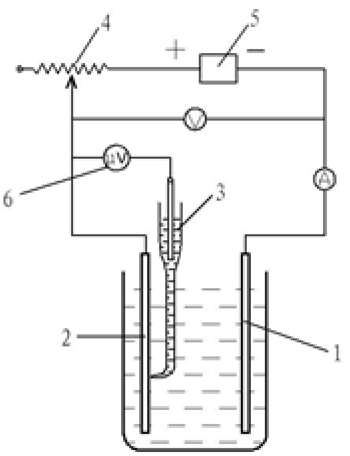

Figure 8. Setup of potential distribution measuring 1. Auxiliary cathode of Al 2. Tested electrode 3. Calomel electrode and associated salt bridge 4. Sliding rheostat 5. Constant voltage DC source 6. Microvolt potentiometer

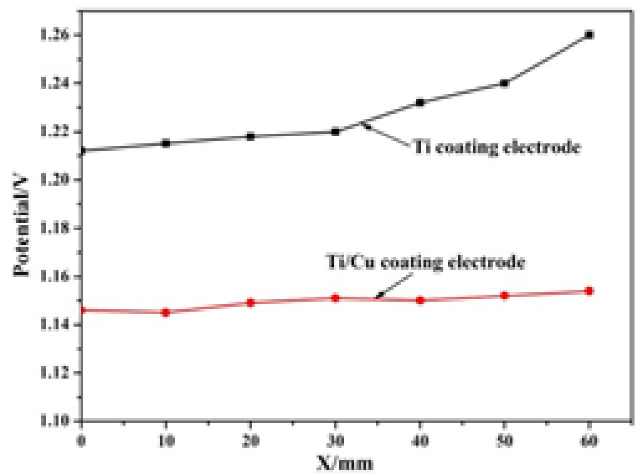

Figure 9. The potential distribution curve chart of different coating electrodes

3.5. The surface potential distribution of the composite materials

It is one of the important indexes which is the distribution of surface potential of electrode materials to study the electrochemical properties of electrode materials in any electrochemical industry, the surface current distribution of electrode material is closely related to the distribution of surface potential, it will influence quality of the product, working process of electrolytic cell and energy consumption of electrode-position process. So, the electrochemical principle of "three electrodes and two return circuits" is used to test the potential distribution of electrode, the experimental schematic diagram shown in Fig. 8.

Fig. 9 is the potential distribution curve chart to coated electrodes of different substrate materials. The surface potential of the Ti/Cu composite coating electrode is obviously lower than that of the pure Ti coating electrode, as follow Fig.9, the potential of Ti-Al composite coating electrode was decreased by 6.6mV to pure Ti coating electrode at the liquid level of electrolyte, that of Ti/Cu was decreased by 8.2mV to pure Ti when the distance is 40mm to liquid level of electrolyte, and that of Ti/Cu was decreased by 11.4mV to pure Ti when the distance is 60mm. That said, the change of the electrode matrix structure can effectively improve the conductivity of the electrode, and electrode over-potential decrease, as the potential has a close relationship with the electro-catalytic activity to electrode materials, the electrode materials had higher electro-catalytic activity when the polarization potential is low[15]. So, the Ti-Al composite coating electrode has high electro-catalytic activity to improve the reaction rate of electrochemical.

And we also can see from Fig.9, the change range of the surface potential was 1.146~1.154V to Ti/Cu composite coating electrode, there is no obvious increase or decrease trend and the change of that is only in the range of 12mV to the distribution of the surface potential. However, the surface potential of pure Ti coated electrode increased from 1.212 V to 1.26 V, its range of voltage change is 48mV within 60mm that is the measurement distance in this study. The change range of surface potential distribution of Ti/Cu material is much smaller than that of other electrode materials. So, the surface potential distribution of Ti/Cu composite coating electrode is more uniform than that of pure titanium. The surface potential distribution is mainly determined by the two part: one is voltage drop(IR) in the electrode material and the other is polarization potential of electrode in electrochemical reaction process. The results from the previous experiment can be seen that the polarization potential of the electrode is related to the electrical resistivity when the polarization reaction occurs in the process of electrochemical reaction, because of different materials have different resistance, different voltage drops are generated when the current passes through the same distance. With the increase of the distance of current, the magnitude of the voltage drop will increase on the electrode surface, for example, its voltage drop is 48mV within 60mm to pure Ti electrode in this study, but the length of the plate is increased by 1.2m in the current commonly used industrial plates, the value of the voltage drop will be greatly increased which caused the distribution of uneven surface current, so that it will have an impact on the actual performance of the electrode.

4. CONCLUSIONS

There are different diffusion reaction products in the diffusion interface to the diffusion reaction layer of Ti/Cu layered composite that was due to the different parameters of preparation process, the phase transition process will occur at the interface with the change of preparation parameters, $CuTi_2$, CuTi, Cu_3Ti_2 and Cu_4Ti are formed the main interface structure by the process of phase transition in the diffusion interface.

It will affect the resistivity of the composites to different preparation process by affecting the composition and structure of the phase in the interface, its resistivity is only 1/15 of pure titanium electrode material. so that it can be improved that is the electrochemical performance of electrode materials. Due to the matrix material added Cu which has excellent conductive properties, he polarization performance of Ti/Cu layered composites is better than that of the traditional pure Ti electrode materials, In electrochemical performance, the polarization potential of the composite decreased about 49~91mV to the polarization potential of pure Ti, the polarization current density of the composite is 1 times higher than that of the pure titanium. And, it also lays the foundation for the uniform distribution of the surface current of Ti/Cu layered composite materials.

5. ACKNOWLEDGEMENTS

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