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Study on the Interface and Performance of Ti-Al Laminated Composite Electrode Materials

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Abstract: *The Ti-Al laminated composite materials had been prepared by hot press diffusion bonding in this article, then, treated for different thickness of Al layer in the same process conditions. The change of composite material structure is influences on the performance of Ti-Al were investigated by SEM, HRTEM, electrochemical workstation and so on. The results show that it has the characteristics of the composite's interface and the completion of "metallurgy like" integration between Ti and Al, the chang of matrix structure design of traditional Ti electrode is good for enhance the electrochemical performance of electrode, it is completely changed how the current transfer on the Ti-Al laminated composite materials, so that current distribution of electrode is uniform.*

Keywords: Hot press diffusion bonding; Ti-Al laminated composite materials; Anode materials; Current transfer mode; Electrochemical performance; Surface potential distribution

1. INTRODUCTION

With the in-depth of human understanding to the sustainable development, the green technology industry and technology has been becoming very important in the current society [1-4]. It puts forward the higher and more severe requirements to save resources, environmental protection and energy saving in the 12th five-year plan. Wet metallurgy industry is a big consumer of resources and environment, and it is also a big energy consumer in nonferrous metal industry, so it has aroused close attention from all walks of life. Moreover, the electrode is the core of the main and important equipment in wet metallurgical industry which is called the "heart" to electrochemical system. And, it is not only affects the rate of electrochemical reaction, but also directly affects the success and failure of the electrochemical reaction process. Therefore, the performance of the electrodes is one of the key factors to the whole electrolytic system[5-7].

Electrode materials provide not only reactive particles for the whole electrochemical reaction system, but also reaction site for the electrochemical reaction, the process of electrochemical reaction depends mainly on the properties of electrode. However, because of the Ti matrix has a high resistance[8] in Ti coated anode material, the current distribution of electrode is not uniform that has become an important factor restricting the development of Ti anode materials[9]. At present, the research mainly concentrated in the deployment of coating material and the failure mechanism of the coating[10-14], but the change of the matrix material structure can play an important role to enhance the performance of electrode material. Consequently, the Ti-Al layered composite electrode materials was prepared by hot press diffusion bonding in this article to increase the conductivity of electrode[15-17], so as to improve the electrochemical performance of electrode. We study that the variety of electrode matrix material has a important influence on internal resistance, speed of electronic transmission in electrode, electrode potential and current distribution through the study on the mechanism of conductivity and mode of current transfer to the composite matrix material.

2. EXPERIMENTAL PROCEDURE

Commercially pure Ti (TA1) and commercially pure Al (L4) were employed in this study. The sizes of the samples were TA1 – 0.8mm×50mm×50 mm, L4 – 4mm×50mm×60 mm. Oxide films of Ti and Al could form easily on each surface. The surfaces of Ti and Al had to be handling before bonding or they would prevent the diffusion of Ti and Al.

The optimum technological conditions to hot pressing diffusion welding process are : bonding temperature,560℃; static pres-

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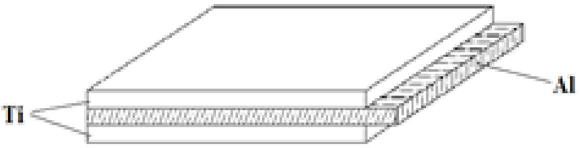

Figure 1. The model of Ti-Al laminated composite material sample

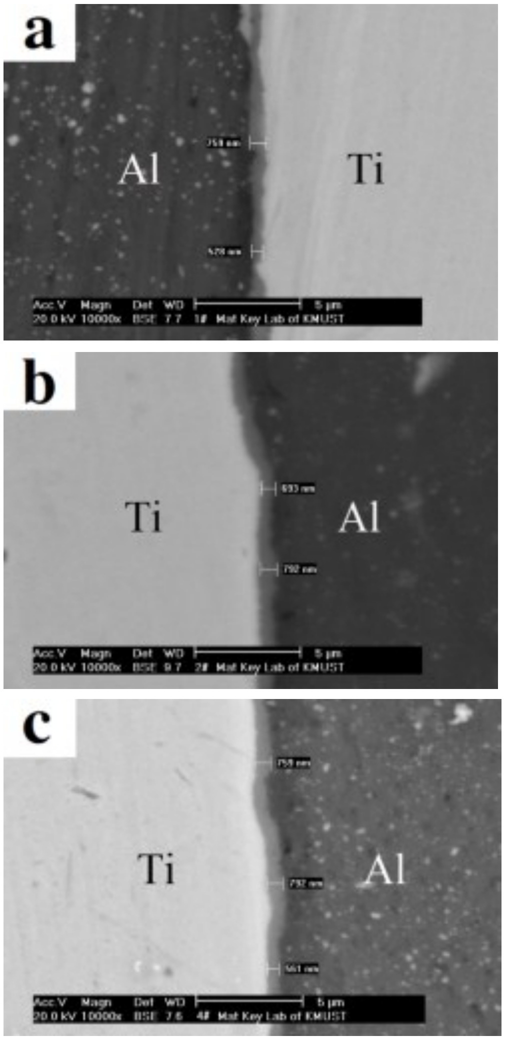

Figure 2. The SEM images of the interface of Ti-Al laminated composite materials with different thickness of Al

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

No.	Al/mm	Ti/mm
1#	2	0.5
2#	4	
3#	6	

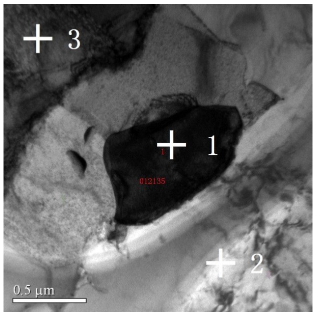

Figure 3. Interface analysis images of Ti/Al laminated composite materials

sure,6MPa; holding time,120min and furnace body for the protection of Ar atmosphere through the pre-exploratory experiments obtained. We study that the variety of matrix material effect on the mode of electrode current transfer by the thickness change of Al plate in laminated composite materials. The change of plate thickness is shown in Table 1, composite electrode material samples as shown in Fig.1.

The microstructures and interface features of the Ti-Al composite materials were observed using a Philips XL-30 ESEM scanning electron microscope (SEM). The interface microtopography was examined in transmission electron microscope (FEI, Tecnai G2 F20) operated at 200 Kv. The electrochemical performance of the Ti-Al composite materials were analyzed using a CHI600A electrochemical analyze instrument.

3. RESULTS AND DISCUSSION

3.1. The microstructure of diffusion zone

Fig.2 shows the SEM images of the interface of Ti-Al laminated composite material which is prepared by hot pressing diffusion welding method and using a different Al thickness under the same condition through changing Al plate thickness.

As you can see from Fig.2, Al reacted with Ti by the diffusion way to form interface diffusion layer that has a certain thickness and continuous stability under the same condition. The diffusion reaction layer is formed between Ti and Al after a series of diffusion reaction, which has the characteristics of the composite's interface and the completion of "metallurgy like" integration between Ti and Al. The width of diffusion reaction layer is about 700nm between Ti and Al under different thickness of Al. Therefore, the change of Al thickness has little effect on the width of diffusion reaction layer.

According to Fick's first law, model of diffusion coefficient and Arrhenius equation[18~19], the width of diffusion reaction layer are related closely to bonding temperature and holding time and the thickness of the material have too little sway over the width of diffusion reaction layer. So, no matter how the thickness of the material changes, the thickness of diffusion reaction layer is similar under the same conditions to hot pressing diffusion welding.

3.2. TEM analysis of the bonding interface of the composite materials

Fig.3 is element content analysis images of fixed-point of Ti/Al

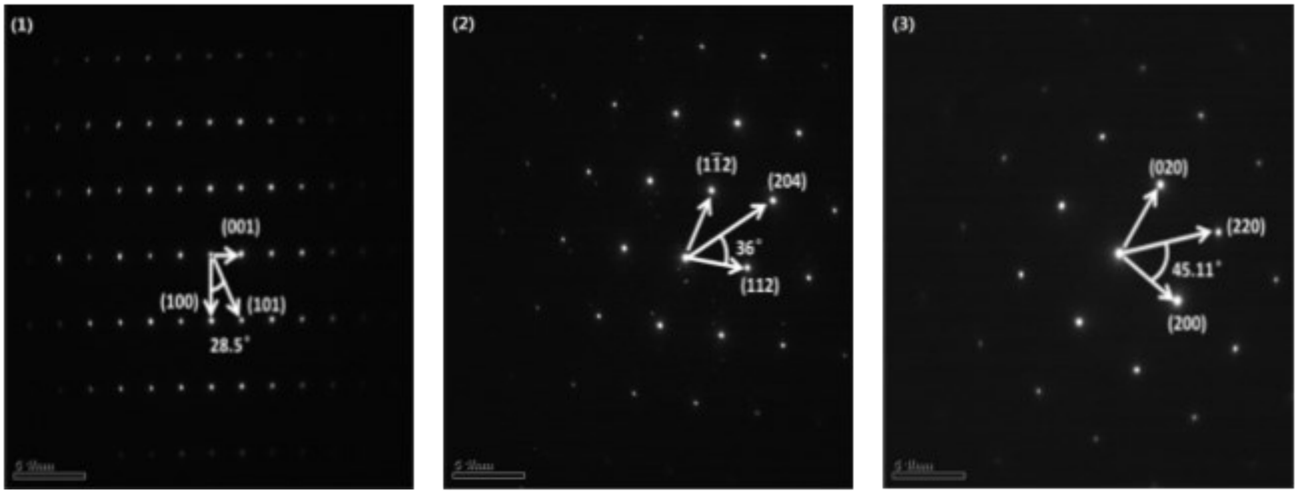

Figure 4. Electron diffraction flowers of matri and interface of Ti/Al laminated composite materias. (1)Ti side; (2) Diffusion reaction layer; (3)Al side

laminated composite materials, the 1 point is particles of the bonding interface in which the atom percentage of Al is 73.67% and that of Ti is 26.33% at the interface, Al: Ti is 2.8:1 to the atom number ratios, and there may be Al_3Ti phase in the bonding interface. The atom percentage of Al is 97.46% in the 2 point, and the atom percentage of Ti is 98.23% in the 3 point in Table 2, so there is Al in the 2 point and there is Ti in the 3 point.

As shown in Fig.4, the high resolution transmission electron microscopy(HRTEM) has been used to test the binding interface of layered composite electrode. Through analyzing the TEM diffraction pattern of Ti-Al layered composite interface, it can be concluded that there is a new phase of matter which is Al_3Ti in bonding interface, and the TEM diffraction patterns are typical lattice diffraction pattern to Ti, Al and Al_3Ti.

According to the above analysis can see, the bonding interface of Ti-Al layered composite are formed by the new large particles of Al_3Ti phases(200-800nm) as follow Fig.3, Ti and Al, there are some the new small particles of Al_3Ti phases(50-80nm) in the gap. The interfacial formation process of Ti/Al layered composites went like this. First, the superimposed structure of the Ti plate and the Al plate is similar to "the sandwich"(as follow Fig.1), the combining state is mechanical type under the influence of stress. With the influence of welding temperature and holding time in the process of hot press diffusion bonding, the heat movement of Al and Ti atoms has already increased, there is the diffusion reaction between Al and Ti, Al_3Ti phase have been found nucleating and growing on the mechanical bonding of Ti and Al, and it kept on increasing, the new Al_3Ti phases are connected to form a continuous diffusion layer at the interface. With the continues of the diffusion reaction, Ti atoms and Al atoms continue to spread to the new phase of the Al_3Ti, and the small particles of Al_3Ti continue to grow to form the large particles.

Table 2. EDS microanalysis of the reaction zone

Location on micrographs	Elements in atom percentage(%)	
	Al	Ti
1	73.67	26.33
2	97.46	2.54
3	1.77	98.23

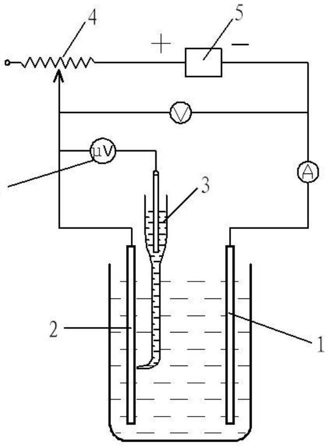

Figure 5. Setup of potential distribution measuring; 1. Auxiliary cathode of Al, 2. Tested electrode, 3. Calomel electrode and associated salt bridge, 4. Sliding rheostat, 5. Constant voltage DC source 6. Microvolt potentiometer

3.2. The surface potential distribution of the composite materials

The potential and current distribution of electrode is very import to electrode-position process in electrochemical industry, it will influence quality of the product, working process of electrolytic cell and energy consumption of electrode-position process. So, the

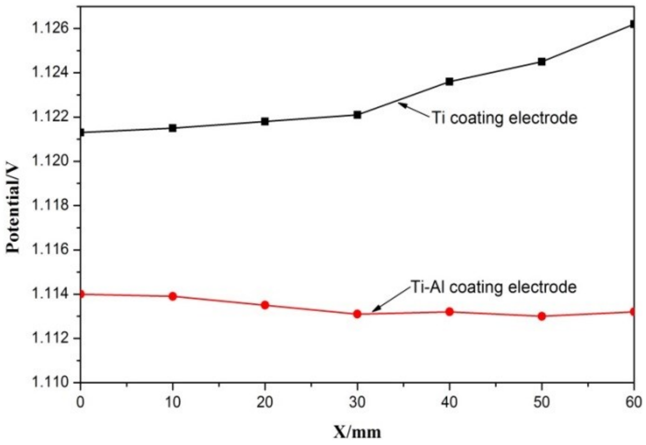

Figure 6. The potential distribution curve chart of different coating electrodes

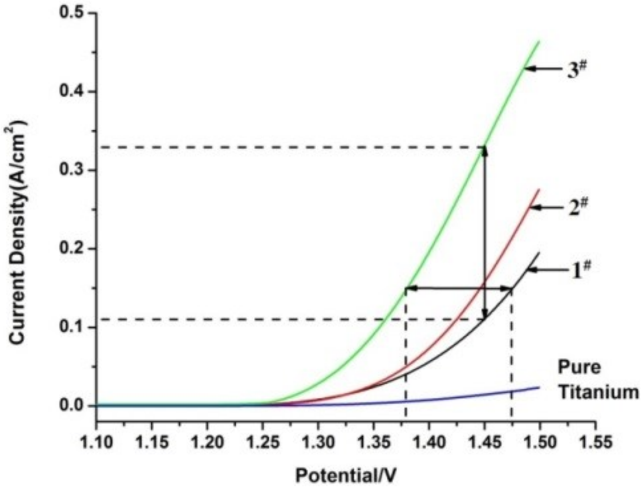

Figure 7. The polarization curve of electrode with Al plate thickness changes

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.5.

Fig.6 is the potential distribution curve chart to coating electrodes of different substrate materials. The surface potential of the Ti-Al composite coating electrode is obviously lower than that of the pure Ti coating electrode, as follow Fig.6, the potential of Ti-Al composite coating electrode was decreased by 7.3mV to pure Ti coating electrode at the liquid level of electrolyte, that of Ti-Al was decreased by 8.3mV to pure Ti when the distance is 20mm to liquid level of electrolyte, and that of Ti-Al was decreased by 10.4mV to pure Ti when the distance is 40mm. 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[19]. 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.6, the change range of the surface potential was 1.1138~1.1153V to Ti-Al composite coating electrode, the change range was 1.1213~1.1262V to pure Ti coating electrode. The electrode potential includes internal resistance voltage drop(IR) and polarization potential(φ) when the connection resistance was neglected. Those polarization potentials(φ) is equal in the same electrolysis, so the surface potential of pure Ti coating electrode is increased that means resistance voltage drop(IR) increases. Its voltage drop is 49mV within 60mm that is the measurement distance in this study, so with the increase of the distance from electrode lugs, its voltage drop will significantly increase. The surface potential distribution of the electrode has a close relationship with the current distribution, and the current distribution depends mainly on the potential distribution when the difference of the local concentration of electrolyte and electrode conductivity is very small. The uneven distribution of the current distribution caused the uneven thickness of the plating coating on the cathode plate surface when the potential is unevenly distributed, even with the appearance of local “burning”. Therefore, the potential distribution will directly affect the current distribution at the surface of the electrode which can lead to localized corrosion and reduce current density during electrolysis. But the potential distribution of Ti-Al composite electrode is relatively uniform, the change range is 1.1135±0.0005V. So, the Ti-Al layered composite electrode helps the potential distribution and the current distribution to homogenize, it improves the utilization ratio to the active material of the electrode coating, reduces cell voltage in the electrochemical process and to prevents side reaction.

3.3. The electrochemical properties of the composite materials

Excellent electrochemical performance has a vital role to the application of electrode material. 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 has the properties curve of the pure Ti electrode in order to comparative analysis.

The electrode is not only the medium of electron motion, but also is the location of electrochemical reaction in the process of electrochemical reaction[21]. It means that the surface of electrode is occurs electrochemical reaction and is passing current when the electrons are transferred, and electronic transfer step closely link electrochemical reaction with current. So, electron transfer steps can improve the performance of the electrode to decrease the over-potential caused by electron transfer. A large number of electrons can gather on the surface of the metal anode to resulting electrochemical reaction about in potential (φ_e) in electrolytic process. According to the kinetics of electrode reaction process[22], the current density of electrode surface is closely related to the over-potential, and electrochemical reaction more easily when it has large current density and has low over-potential.

As you can see from Fig.7, Ti-Al laminated composite electrode is better than pure Ti anode in the polarization performance. They have similar polarization curve to composite electrode with different Al thickness. When the potential is less than 1.25V, almost no

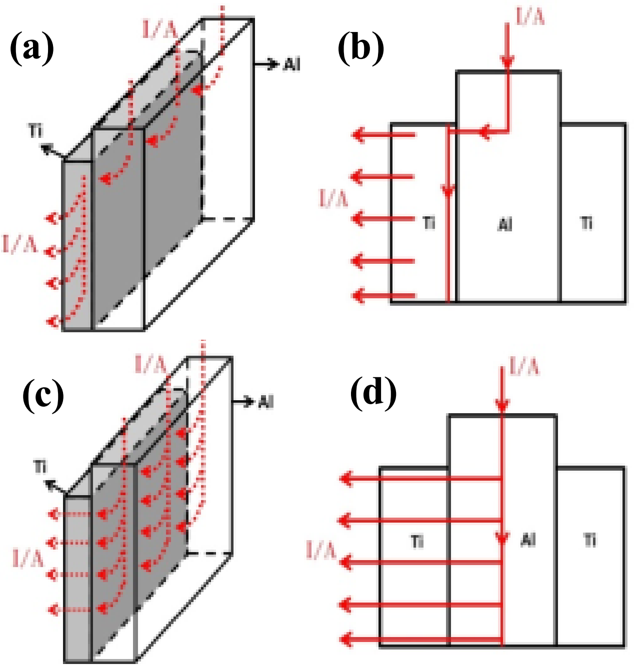

Figure 8. The diagrams of direction of Current in composite electrode; (a) The principle of shortest distance; (b) The simplified diagram of the principle of shortest distance; (c) The principle of minimum energy; (d) The simplified diagram of the principle of minimum energy

current through the electrode surface, but when the potential is greater than 1.25V, 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. The polarization curves of the composite electrode materials gradually move to right with the increase of Al thickness. In Fig.7, when the current density of electrode is 0.15A/cm^2, the polarization potential of 1$^{\#}$ electrode sample is about 1.475V, that of 3$^{\#}$ electrode sample is about 1.38V, the polarization potential is decrease by 95mV, it shows that the catalytic activity of the composite electrode is improved with the increase of Al thickness, and the slot voltage of composite plate is low with the increase of Al thickness under the same current density. Furthermore, when the current density of polarization potential is 1.45V, the current density of 1$^{\#}$ electrode sample is about 0.11A/cm^2, that of 3$^{\#}$ electrode sample is about 0.33A/cm^2, and the current density of 3$^{\#}$ sample has three times better than that of 1$^{\#}$ with the increase of Al thickness, it means that the current density of composite plate can pass the bigger and better conductivity.

The electrochemical catalytic activity of electrode will be increased 10 times when the electrode over-potential is decrease by 100mV[21].So, we can see in this research that it can improve the electrochemical catalytic activity of electrode by the increase of Al thickness in Ti-Al laminated composite. It can be seen from the interface morphology of Ti-Al composite combining with Fig.2, thanks to the resistance of substrate and structure have a certain impact on the transmission mode of current on the electrode in laminated composite, and the electrochemical performance is affected by the Al matrix thickness in Ti-Al laminated composite.

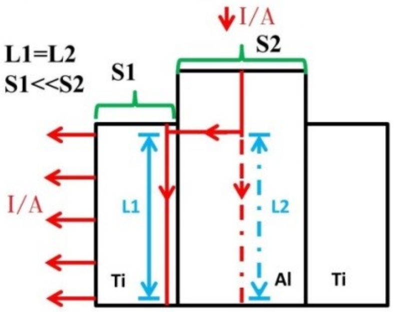

Figure 9. The longitudinal transmission of current in composite electrode

3.4. Mechanism analysis of current transfer composite electrode

The current passes from pole ear to surface into the electrolyte in the actual process of electro-deposition, yet the current passes from middle layer (Al) to surface into the electrolyte in laminated composite electrode. And, the transmission process and mode of current are also related to the electrochemical performance of electrode. The transmission mode of current is simplified as a linear pattern in this research, we can divide that into two types according to both the transmission path, “the shortcut principle”(in Fig.8 (a) and (b)) and “the minimum energy principle” (in Fig.8 (c) and (d)).

The polarization properties of electrode can be good or bad, depending on the conductivity of matrix material. The matrix conductivity is better and the negative shift of polarization curve is more. According to the resistance formula as follow:

$$R=\rho L/S \tag{1}$$

where ρ is the material resistivity with Ωm, L is the material length with m, S is the cross-sectional area with m^2.

By the formula (1) shows that the longer length of conductive body and the more resistance, the larger cross-sectional area and the smaller resistance. The resistivity of Ti($4.2\times10^{-1}\mu\Omega m$) is 17 times as high as that of Al($2.83\times10^{-2}\mu\Omega m$) in 20ºC[23]. The residual resistance of intermetallic compound is about $2\times10^{-1}\mu\Omega m$ at the interface between Ti and Al in 4.2K, and its resistivity is about $5\times10^{-1}\mu\Omega m$ in 273K, its resistivity values is with the similar that of Ti, so the interface layer together into the Ti side according to the resistivity to simplify the calculation. There are two main types of current transmission in the composite electrode: longitudinal transmission to the matrix depth and transverse transmission to the surface of matrix.

3.4.1. Longitudinal transmission methods of matrix current

The sketch map of longitudinal transmission is in Fig.9 for the "the shortcut principle" and "the minimum energy principle" in Fig.8. We know by the resistance formula that the distance of longitudinal transmission is L, L1 is equal to L2 in Fig.9. When the cross-sectional area of Ti side is equal to Al, it depends on the resistivity of Ti and Al to the resistance of longitudinal transmission

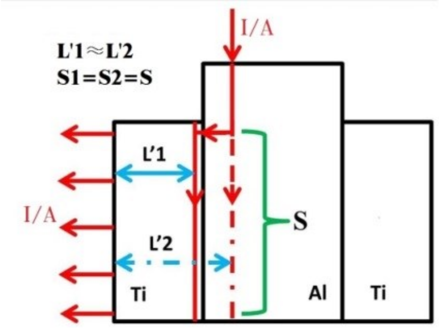

Figure 10. The horizontal transmission of current in composite electrode

current, the resistance of current transmission is 17 times at Ti side as high as it is at Al side. According to Table 1, the cross-sectional area of Al is much larger than the cross-sectional area of Ti in the composite matrix, so the resistance of Ti is 17 times far higher than that of Al.

3.4.2. Transverse transmission methods of matrix current

The sketch map of transverse transmission is in Fig.10 for the "the shortcut principle" and "the minimum energy principle" in Fig.8. We know by the resistance formula that the resistance is depends on the distance of transverse transmission (L') when the cross-sectional area of Ti side is equal to Al, L'1 is equal to L'2 in Fig.10. Therefore, the resistance of transverse transmission are approximately equal in the composite matrix to the "the shortcut principle" and "the minimum energy principle".

Above all, the direction of the current is always flows to the minimum resistance in longitudinal transmission methods when the resistance of transverse transmission is equal, so the mode of current transfer is the "principle of minimum energy" as shown in Fig.8 (c) and (d), that the current passes from middle layer (Al) to the surface of Ti, and into the electrolyte flow out from the surface of Ti in laminated composite electrode. As can be seen from the Fig. 2 and Fig. 7, the polarization curves of the composite electrode materials gradually move to right with the increase of Al thickness. It is prove that the key factor is change the mode of current transfer to improve the electrochemical properties of composite electrode. Moreover, the distribution of current in low resistance material is more uniform than that in the high resistance material.

4. CONCLUSIONS

No matter how the thickness of Al changes, the thickness of diffusion reaction layer is similar under the same conditions to hot press diffusion welding. By changing the structure of the electrode matrix, it can realize the uniform distribution of current, and improve the catalytic activity of the electrodes.

The mode of current transfer is the "principle of minimum energy" in Ti-Al laminated composite electrode, the inner core metallic Al is a collector carrier and conducting path, and the outer layer metal Ti remains electrochemical properties of "valve metal", the mode of current transfer is passes from middle layer (Al) to the surface of Ti and into the electrolyte flow out from the surface of Ti in laminated composite electrode. Moreover, the mode of current transfer is the basis to the uniform current distribution.

5. ACKNOWLEDGEMENTS

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