Corrosion Behavior of Diffusion Bonding Joints of (OFHC) Copper with Stainless Steel 304L in 3.5% NaCl

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Abstract

The present work deals with direct diffusion bonding welding without interlayer of austenitic stainless steel type AISI 304L with Oxygen Free High Conductivity pure copper (OFHC) in vacuum atmosphere ($1.5 *10^{-5}$ mbr.). The optimum bonding conditions are temperature of 650 $^\circ$C, duration time of 45 min. and the applied stress of 30 MPa, in order to secure a tight contact between the mating surfaces. The corrosion behavior of diffusion bonding joints in 3.5% Nacl is studied to evaluate the corrosion resistance of welding joints by using Potentiodynamic method. The observed microstructure of corroded specimen of optimum diffusion bonding joint shows that the corrosion current density has low value as compared with base materials used. During polarization, galvanic coupling is observed between two materials used. At passivity region, inverse polarity is occurred at 450mV. Therefore, passive stainless steel 304 L behaves as cathode respective to pure copper, the corrosion behavior of the diffusion bonding joint was mostly by copper side. The corrosion results indicate the presence of galvanic effect. The corrosion current density of copper, stainless steel 304L and bond joints condition were (3.66 μA/cm^2, 1.62 μA/cm^2 and 1.85μA/cm^2) respectively. A SEM examination of corroded diffusion bonding joint indicates that the galvanic corrosion happened on copper side. The corrosion rate of bonding joint conditions was 0.85 mpy, which is less than 1%. This means that corrosion resistance of bond joint is more than excellent.

1. Introduction

The joining of dissimilar metals is difficult due to their different physical, mechanical and chemical properties that govern the interaction between the metals and new phases that formed. In joining of dissimilar metals it is important to take in account the changes brought by fusion welding in the chemical analysis of the metal adjacent to parent metals [1]. Fusion welding techniques for joining materials are becoming difficult, because it is necessary to control the melting on both sides of two materials together due to the required differences of the physical properties such as; thermal expansion, melting temperature and thermal conductivity. [2, 3]. A fusion welding process will be faced problems by defects like; porosity, weld cracks and segregation, and to overcome on these problems, joining dissimilar metals can be used by a welding process in the solid state [4]. The direct diffusion joining of two materials are utilized in this work in vacuum furnace of almost (1.5 * 10^{-5}mbr) to achieve a sound diffusion joint between two metals, therefore it can be studied the corrosion behavior of the welding joints in (3.5% Nacl).

2. Experimental Work
2.1 Materials and Bonding Procedure

Materials used in this research were wrought austenitic stainless steel AISI 304L according to (ASTM volume 01.01) [5] and hard drawn pure copper (OFHC) according to (ASTM volume 02.01) [6]. The chemical compositions of two base materials used are shown in Table (1). The materials to be joined by diffusion bonding were pure copper(OFHC) and stainless steel 304L. Cylindrical samples of 15mm diameter for each lengths were used with 30 mm and 60 mm for copper and stainless steel respectively[7]. The mating sample surface was prepared using convential grinding on 1200 grade SiC papers followed by polishing with diamond paste using maufacturing holder to get flat surface . The specimens were cleaned in ultrasonic bath using acetone for 15 min. to remove adhered contaminations and dried in air before bonding.

2.2 Preparation of Vacuum Diffusion Bonding System

In order to evaluate the sound diffusion bonding of two dissimilar materials of pure copper (OFHC) and austanitic stainless steel type AISI 304L, the diffusion bonding requires to be applied in vacuum. Joining under vacuum reveals

minimum impurity content, even in the case of high reactive metals. Vacuum provides for faster and more complete degassing of materials being joined and the removal of oxides, impurities and contaminants from both the surface and the bulk materials. Therfore ,diffusion bonding unit is buit in the University of Technology, Production Engineering and Metallurgy Department. The system consists of vacuum diffusion pump, double stage rotary vacuum pump, electrical loading system with capacity of 50 ton, vacuum tube furnance with heating system, vacuum fitting and cooling system for furnace and diffusion. The whole unit is shown in Fig.(1).

Table (1): Nominal and analytical chemical composition of stainless steel and Copper.

Element	Nominal Value (Wt. %)	Analytical Value (Wt. %)
Stainless Steel		
C	≤ 0.03	0.024
Cr	18-20	18.230
Ni	8-11	8.020
Si	≤ 1.00	0.37
P	≤ 0.045	0.042
Mn	≤ 2.00	1.56
S	≤ 0.030	0.024
Fe	balance	balance
Copper		
Cu%	99.95	99.938
Cr%	0.001	0.001
Fe%	0.0003	0.0005
Sn%	0.01	0.0196
Mn%	0.0002	0.0003
Si%	0.00005	0.00005
Co%	0.0005	0.0005

Figure (1) The Vaccum Diffusion Bonding Unit.

2.4 Electrochemical Tests

The specimen with dimensions of (20mm*20mm) was cut from the bonded samples and prepared as in the microstructure test (only grinding and polishing was used), then the specimen put in the holder. The holder was immersed in the solution of 3.5 wt. % NaCl and a surface area of one square centimeter of the specimen was exposed to the corrosive solution. The stainless steel 304L, pure copper and bonding joint specimens were used as working electrode. The reference electrode was a saturated calomel electrode (SCE), and all potentials were referred to this electrode. A platinum electrode was used as the counter electrode. The specimen was connected to a copper wire and then embedded into an epoxy resin. Before measurements were taken, electrode was grounded with emery paper up to 1200 and polished, and then washed thoroughly with distilled water. Finally, the working electrode was cleaned ultrasonically for 10 minutes in acetone. Then it was immersed in the test solution until the potential was stable and had constant value. The open circuit potential for copper was -160 mV while for stainless steel was -260 mV. The Potentiodynamic polarization test was carried out using a computer potentiostat type M-Labsci. The three-electrode electrochemical cell is the standard laboratory apparatus for the quantitative investigation of the corrosion properties of materials used in this work. The first electrode is the working electrode (W.E.). The working electrode is the name given to the electrode being tested (the specimen). The net surface area of the specimens that were used for both O.C.P- time and Tafel extrapolation measurements were exposed to seawater solution equal to 1 cm^2. The temperature of the polarization cell was maintained at temperature of 30 °C. The full time period for O.C.P-time test was 30 minutes .The polarization was obtained by scanning the potentials from -250 OCP to +500 from O.C.P at scanning rate 10 mV/min.

3. Results and Discussion

The maximum tensile strength of bonding joint was obtained at the bonding conditions of temperature at 650 °C, duration time of bonding at 45 min. and applied load of complete coalescence at 30 MPa. [9]. Joint efficiency is attributed to the quality of the joints. Joint efficiency is the numerical value expressed as the ratio of the yield strength of welded joint to the yield joint of the parent metal [8].

Joint efficiency = 153 MPa/ 230 MPa (for copper) % = 66.5%

3.1 Microstructure of diffusion bonding joints

Good results were obtained for almost all the diffusion bonding joints specimens under various

bonding conditions between (OFHC) hard drawn pure copper and austenitic stainless steel type 304L. The specimens were bonded at temperature of 650 °C for duration time of 45 min. and stress of 30 MPa was applied as optimum bonding conditions [9]. Adequate temperature, time and applied stress are important for diffusion of atoms in diffusion bonding welding process. Diffusion requires enough time to occur and if large numbers of atoms are to be diffused in order to get on a uniform structure long time is needed even at high temperature [10].

A typical cross-sectional micrograph of diffusion bonding joints of austenitic stainless steel AISI 304L with hard drawn pure copper (OFHC) is shown in Fig. (2). The inter diffusion zone was observed and formed metallic bonding between two base materials after post heat treatment at 800 °C for 30 min. to homogenize the structure and decrease the residual stress during diffusion bonding welding process as shown in Fig. (4).

The fracture of almost tensile test specimens which happened on the copper side not at the bond line is shown in Fig. (3). This means the bond area is much stronger than copper side, this may be due to the used vacuum atmosphere conditions which result in complete mating of two surfaces, diffusion of copper atoms leads to good bonding.
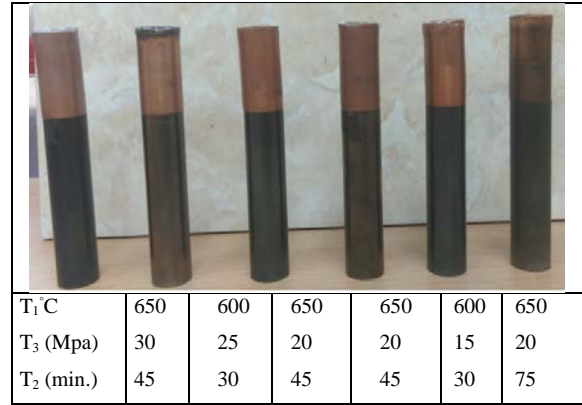

T_1°C	650	600	650	650	600	650
T_3 (Mpa)	30	25	20	20	15	20
T_2 (min.)	45	30	45	45	30	75

Figure (2): A set of diffusion bonding joints at different bonding conditions.
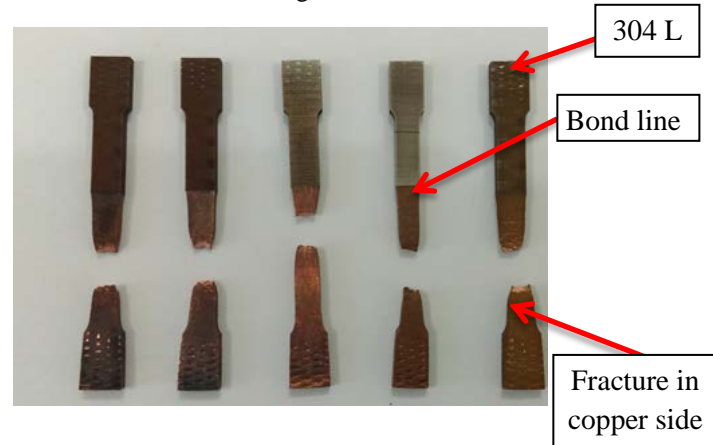

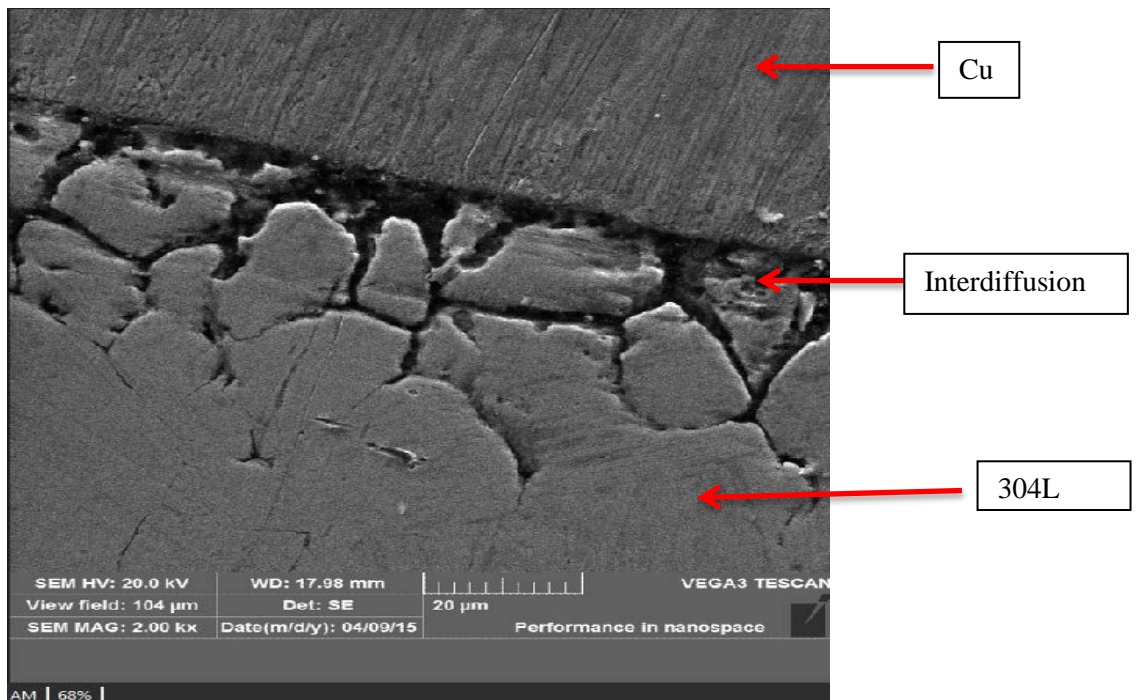**Figure (3)** Fracture of Diffusion Bonding Joints.

Figure (4): SEM Micrograph of diffusion bonding joint.

3.2 Corrosion Behavior

A study of electrochemical behavior of base materials involves comparing the results with diffusion bonded joints to assess the corrosion resistance of bonded joints in 3.5% NaCl. The O.C.P and Potentiodynamic polarization are measured to give an indication of the corrosion behavior of diffusion bonding joints. The Potentiodynamic polarization test was carried out using a computer potentiostat type M-Labsci shown in Figure (5). The three-electrode electrochemical cell is the standard laboratory apparatus for the quantitative investigation of the corrosion properties of materials used in this work. The first electrode is the working electrode (W.E.). The working electrode is the name given to the electrode being tested (the specimen). The net surface area of the specimens that were used for both O.C.P- time and Tafel extrapolation measurements were exposed to seawater solution equal to (1 cm^2).

**Figure (5):** Photograph of Corrosion Test Device.

3.2.1 Open Circuit Potential (O.C.P)

Determination of the open circuit potential (O.C.P) time curves of specimens in 3.5% NaCl at room temperature under different bonding conditions are shown in Table (2) for base materials (hard drawn pure copper and stainless steel 304L) and different diffusion bonding conditions;(A) 650 °C, 45 min. and 30 MPa load;(B) 650 °C, 45 min. and 10 MPa;(C) 650 °C, 75min and 20MPa. These values of the O.C.P may be fixed after duration time of 30 minutes. From the values in Table, the O.C.P has shifted to more negative as compared with the copper, but the nearest values to the copper was at optimum bonding conditions of 650 °C, 45 min. and 30 MPa load. Therefore, load increase leads to

decrease in the tendency for corrosion at constant temperature diffusion bonding.

Table (2): Open Circuit Potentials in 3.5%NaCl

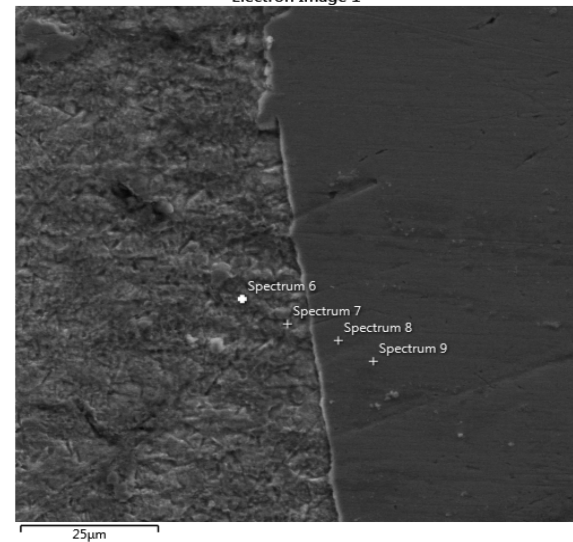| Materials	Open Circuit Potential (O.C.P)(mV)
Copper(OFHC)	-160
Stainless Steel (304L)	-204
A(650 °C, 45 min., and 30MPa)	-184
B(650 °C, 45 min. and 10MPa)	-229
C(650 °C, 75 min. and 20MPa)	-185.6
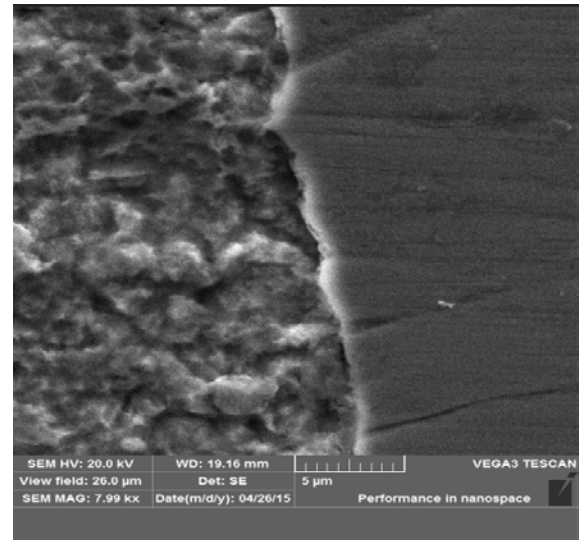
Electron Image 1

Figure (6): Micrograph of diffusion bonding after corrosion test
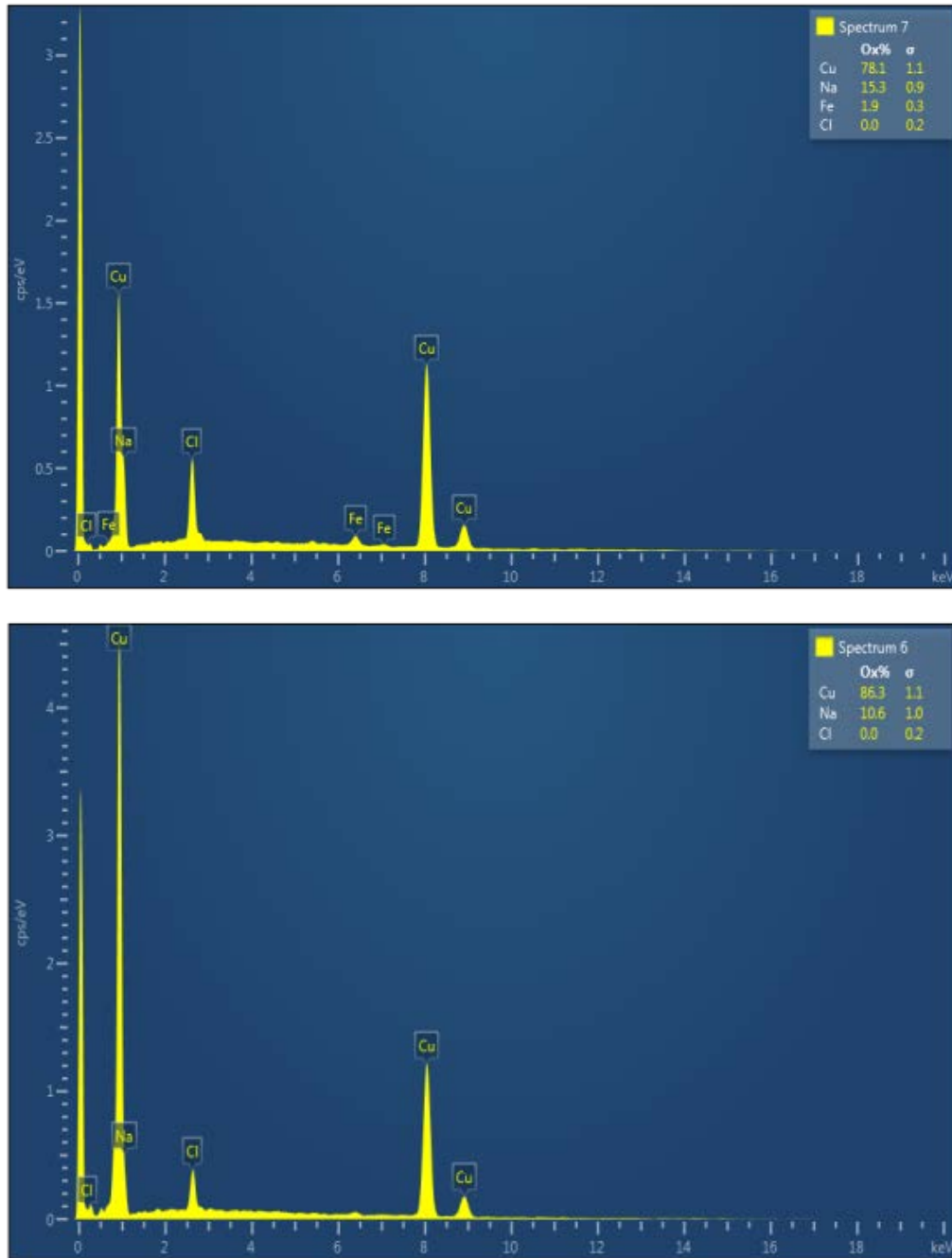
Figure (7): EDS analysis at optimum bonding condition.

3.3 Potentiodynamic Polarization Curves
3.3.1 Potentiodynamic curves of base material.

Typical Potentiodynamic curves of austenitic stainless steel 304L and pure copper (OFHC) in 3.5% NaCl are shown in Fig. (8).

Figure 8 represents the potentiodynamic curves for base materials which indicate that the corrosion potentials of pure copper (OFHC) and stainless steel 304L are (-158.3 mV) and (-239.3mv) respectively. At the first stage of polarization curve in the anodic region the behavior of stainless steel 304L is an anode and the copper behavior as cathode respectively to galvanic series in seawater. But when the stainless steel 304L is passivated by coated with natural oxide film on the surface of stainless. The stainless steel at this location behave as cathode due to formation of film on stainless steel and copper behaves as anode and this can be seen clear according to the galvanic series of metals in seawater. The passive stainless steel will be behaved as cathode respective to pure copper. This inverse polarity happened at 450 mV. As shown in Fig. (8 a). The stainless steel has two locations as compared with copper. For this reason, we can see the corrosion happened at the copper side not at the stainless steel or bonded joints area because of the formation of solid

solution and solution has low corrosion rate as compared with base materials used.
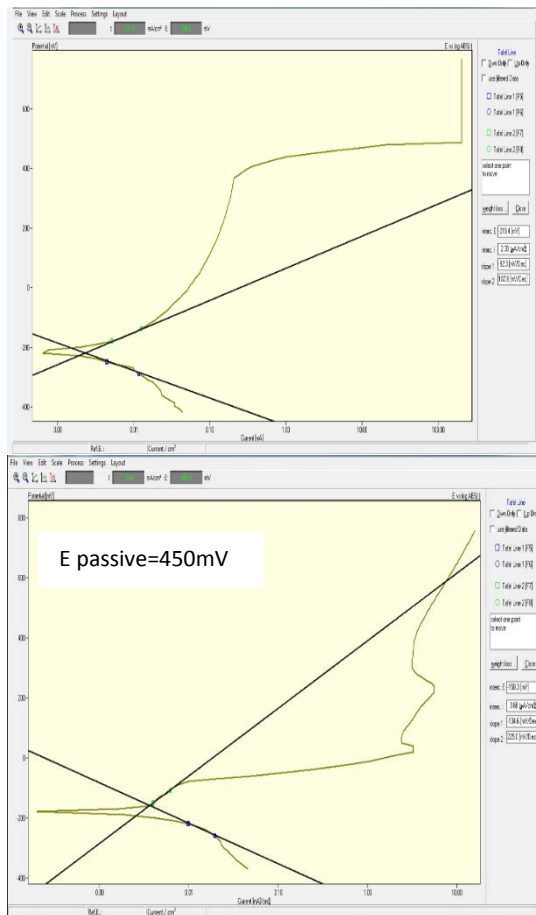

E passive=450mV

Figure (8): Potentiodynamic curves of base materials (a) 304L (b) Copper

Table (3): Corrosion results of testing specimens.

Mater ials	Ecorr (mv)	icorr ($\mu A/cm^2$)	-βc (mv/Dec)	+βa (mv/Dec)
Cu	-158.3	3.66	134.6	225
304L	-239.3	1.62	83.1	99.4
A	-188.5	1.84	84.5	119.9
B	-229.7	10.8	150.4	125
C	-195.6	4.85	108.2	127.3

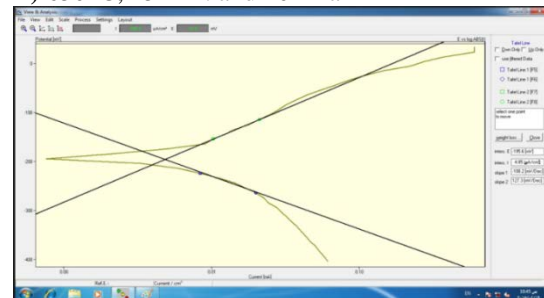## 3.4 Potentiodynamic polarization curves of diffusion bonding joints

The potentiodynamic curves of optimum diffusion bonding joints were studied in 3.5% NaCl to evaluate the corrosion behavior of these joints in this solution and to calculate the corrosion rate of diffusion bonding joints. The Potentiodynamic polarization curves for various bonding conditions are shown in Fig. (9).
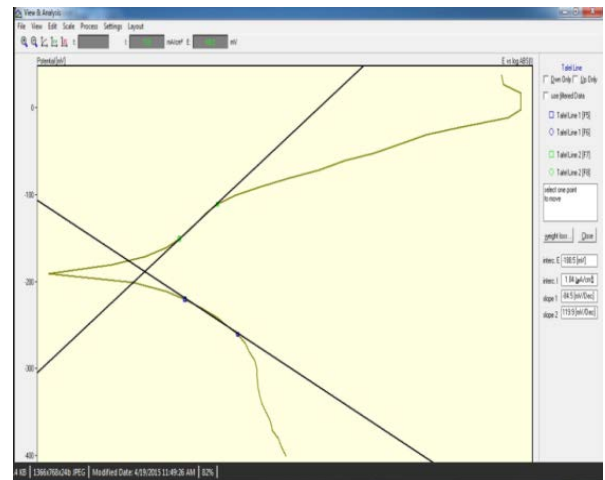
A) 650 $^\circ$C, 45 min and 30 MPa
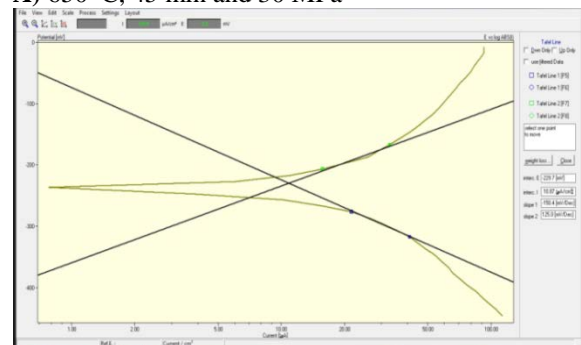
B) 650 $^\circ$C, 45 min. and 10MPa

C) 650C$^\circ$, 75 min. ,20Mpa

Figure (9): Potentiodynamic polarization curves of diffusion bonding joints

Figure (9 A) shows minimum corrosion current density of (1.84mA/cm^2) for diffusion bonding joints at temperature of 650 $^\circ$C, duration time of 45 min. and applied load of 30 MPa. The corrosion behavior of welding joints at the same temperature and duration time with low applied stress indicates higher corrosion current density of (10.8mA/cm^2), compared with previous case as shown in Fig. (9 B). This means that the applied load reveals complete micro deformation of asperities and increases the area of contact between two matting surfaces   Fig. (9 C) represents the corrosion behavior of diffusion bonding welding joints at the increase in duration time which leads to low corrosion current density of (4.85mA/cm^2) as compared with effect of load.

3.5 Corrosion rate and polarization resistance

Corrosion rate of diffusion bonding joints after corrosion test was calculated using equation (1) [11]. The equation parameters were evaluated for the corrosion area by EDS to find out the elements which can be observed in this area. Fig. (7) indicates that most welding area consists of copper, therefore copper data can be used to calculate the corrosion rate and polarization resistance by using equation (1) and (2). The corrosion rate and polarization resistance values are shown in Table (4).

$$C.R \ (mpy) = \frac{0.13 \times E.w \times icorr}{\acute{\rho}} \ ... (1)$$

$$Rp = \frac{ba * bc}{2.303(ba + bc)icorr} \ ... (2)$$

Table (4) Corrosion Rate and Polarization Resistance

Materials	icorr (μA/cm^2)	-βc (mv/Dec)	+βa (mv/Dec)	Rp (Ω/cm^2)	C.R (Mpy)
copper	3.66	134.6	225	10	1.689
304L	1.62	83.1	99.4	12	0.671
A	1.84	84.5	119.9	11.7	0.8495
B	10.8	150.4	125	2.7	4.986
C	4.85	108.2	127	5.24	2.239

4. Conclusions

1- The maximum tensile strength of diffusion bonding joint was observed for diffusion bonding joint at optimum bonding conditions of 650 °C, 45 min., and applied stress of 30 MPa, annealed at temperature of 800 °C, for 30 min.

2- The maximum depth of interface is equal to 11.80 μm.

3- The corrosion rate of diffusion bond at optimum bonding conditions was equal to 0.85 mpy and is less than obtained for copper and more than corrosion rate of austenitic stainless steel 304L.

4- The formation of solid solution phase at the bonding joints between copper and nickel was observed which leads to low corrosion rate of optimum bonding joint condition.

5- The passive of stainless steel 304L will be behave as cathode respective to pure copper. This inverse polarity happened at 450mV.

References
[1] Ziegelhem j., Hiraki S., Diffusion bonding of Similar/dissimilar light metal sheet, Journal of Material Process Technology, (2007)

[2] G. Mahendran, Balasubramania V., "Influences of diffusion bonding process on bond characteristics of Mg-Cu dissimilar joints", Trans. Nonferrous Metall., (2010).

[3] J. Grum, Slabe J. M," The use of design and response surface methology for fast determination of optimal heat treatment conditions of different Ni-co-Mo surface roughness layers", Journal of Material Processing Technology, (2014).

[4] B. Ravisankar, Ramakishnan S.S., Angelo P. C., On diffusion bonding of Ti-6Al-4V, Transactions of Indian Institute of Metals, (2002).

[5] ASTM Handbook,Iron and metal products,vol. 01.01, (1989).

[6] ASTM Handbook,Non-Ferrous metal products,vol. 02.01, (1989).

[7] Ahmed Ali Akber Akber, "Diffusion Bonding of Oxygen High Conductivity Copper to Austenitic Stainless Steel" PhD thesis, University of Technology, (1996).

[8] S.Assarzadeh and Ghoreishi, Statistical Modeling and Optimization of the EDM Parameters on Wc-6% Co Composite through hybrid response surface methodology-desirability function approach, International Journal of Engineering Science and Technology, (2013).

[9] Safaa Mohammed Hassoni, "Characterization of Diffusion Bonding Joints of Oxygen Free High Conductivity (OFHC) Copper with Stainless Steel 304L" PhD. Thesis, University of Technology, (2015).

[10] M. Balasubramanian, Application of Box-Behbken design of fabrication of titanium alloy and 304 stainless steel joints with silver interlayer, Materials and Design, (2015).

[11] ASTM Handbook, Wear and Erosion, vol. 03. 02, G 102, (1999).

سلوك التاكل للربط الانتشاري للنحاس النقي(OFHC) و الحديد المقاوم للصدأ في 3.5% Nacl

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الخلاصـــة

الدراسة الحالية تتعلق بتوصيف الربط الانتشاري المباشر للنحاس خالي الأوكسجين عالي الموصلية مع الصلب المقاوم للصدأ الاوستنايتي نوع(304L) مختبريا. وقد تم ربط المعدنين في جو مفرغ يصل الى ($1*10^{-5}$ mbr) ولأجل ذلك تم تصنيع منظومة ربط انتشاري لتحقيق الجو الفراغي المطلوب. حيث كانت الظروف المثلى للربط هي عند درجة حراره $650^{\circ}C$ وزمن ربط 45 دقيقه والجهد المسلط كان 30 ميكاباسكال. ولمعرفة قوة الربط تم اجراء فحص الشد لمنطقة الربط حيث كانت متانة الربط عند ظروف الربط المثلى تساوي 153 ميكاباسكال وذات كفاءة ربط 66.5% مقارنة بالنحاس. وبعد ذلك تم دراسة التاكل لوصلات الربط الأنتشاري المثلى في محلول فعال من3.5% لمعرفة مقاومة التاكل لمنطقة الربط وتبين ان منطقة الربط عند ظروف الربط المثلى ذات معدل تاكل يساوي (0.8495 mpy) وهو اقل من معدل تاكل النحاس (1.689 mpy) واكثر بقليل من معدل تاكل الصلب المقاوم للصدأ (0.671 mpy) وهذا يدل على ان تاكل منطقة الربط الانتشاري هو اقل مما يعني ان مقاومة تاكل منطقة الربط كانت فوق الممتازة.