

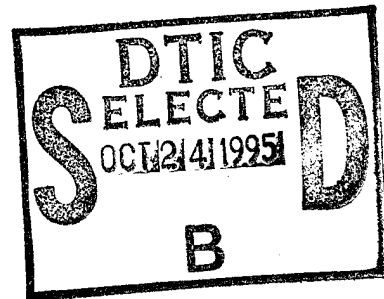
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CONTACT CORROSION BETWEEN CARBON FIBER REINFORCED
COMPOSITE MATERIALS AND HIGH-STRENGTH METALS

by

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CONTACT CORROSION BETWEEN CARBON FIBER REINFORCED COMPOSITE MATERIALS AND HIGH-STRENGTH METALS

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Abstract: Experimental results show that when carbon fiber/epoxy resin composite materials are joined with high-strength titanium alloys, aluminum alloys, 1Cr18Ni9Ti stainless steel, or other structural materials, galvanic corrosion and crevice corrosion take place on the contact boundaries. This corrosion is primarily determined by the electrochemical properties of the materials. It is also related to the materials' mutual coupling situation, treatment technology, and environmental conditions. Galvanic corrosion is affected by the coupled materials' static energy of corrosion (E_{corr}), galvanic currents, and other dynamic closed-circuit properties. In a 3.5% NaCl solution, materials' electrochemical properties and treatment techniques tended to have similar effects on galvanic corrosion and crevice corrosion. When soaking weight loss methods, salt spray methods, and crevice corrosion methods were used to test couples of CFRM with anodized titanium alloys or couples of CFRM with hot water-sealed or chromate-sealed aluminum alloys, the materials were proved to be stable and satisfactory for the needs of engineering applications.

Key words: carbon fiber reinforced composite materials (CFRM), high-strength metals, contact corrosion, crevice corrosion

The applications of carbon fiber reinforced resin-based composite materials in aircraft and spacecraft have clearly reduced structural weight, but contact corrosion between CFRM and high-strength structural components, as well as other failure phenomena brought about by surface properties, seriously affect the life spans and reliability of aircraft. A great deal of research has already been done on galvanic corrosion and crevice corrosion produced between different kinds of materials⁽¹⁻⁴⁾. Today, resin-based carbon fiber reinforced composite materials are widely used

materials to connect with aluminum alloy fuselages, high-strength steel beams, titanium alloy junctions, and other frequently used structural parts is a problem of widespread concern in aviation and spaceflight circles.

1. Research methods

The materials used in this experiment were carbon fiber reinforced resin-based composite materials, high-strength titanium alloys (TA1, TA7, TC1, TC4), high-strength aluminum alloys (LY12CZ, 7075T76, LC4CS), and stainless steel (1Cr18Ni9Ti). After the aluminum alloys were anodized, their surfaces were treated with either a chromium sealing method that used chromate sealing or a water sealing method that used hot water sealing, to raise their corrosion resistance; in addition, a polyurethane varnish was spread on their surfaces as a protectant. The titanium alloys were also anodized.

A FDO-2 galvanic corrosion testing instrument was used to determine the (open circuit) energy of corrosion E_{CORR} and $E_{\text{CORR}}-t$ (energy of corrosion minus time) curves of the materials being researched, the I_g-t (galvanic energy minus time) curves of coupled samples, and their I_g-t (galvanic current minus time) curves. The medium used in this experiment was a 3.5% NaCl aqueous solution⁽⁵⁻⁷⁾.

A weight loss method was used to determine the volume of coupled materials in solution: samples with surface area (ml/cm^2) greater than 20 were in a 5% NaCl solution, the medium was kept at $37 \pm 1^\circ\text{C}$ with a pH value of 6, and the amount of weight lost by the materials after soaking for 72 hours [was used to] assess their corrosion resistance grade. The above metal research materials were divided into protected and non-protected groups, and were separately organized into couples with research materials.

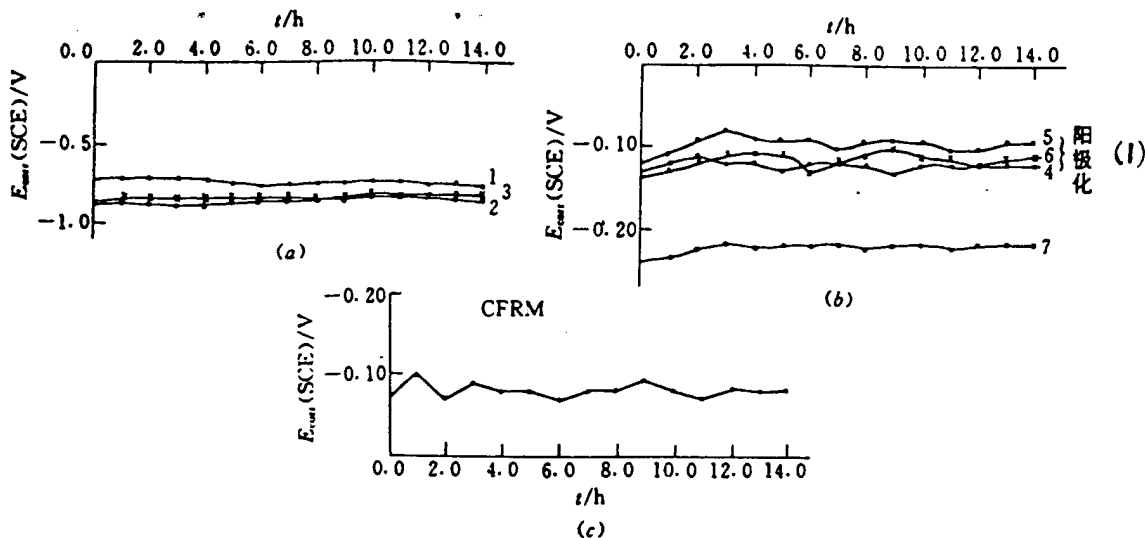
Samples of the above different materials were placed in a salt spray box and, after being sprayed continuously for 168 hours with a $35 \pm 1^\circ\text{C}$, pH 6-6.5, 5% NaCl aqueous solution, were taken out and weighed, and the couples' salt spray corrosion resistance grade was determined according to the amount of weight they lost.

A crevice corrosion test was carried out on the pairs of materials based on the crevice samples recommended for use by ASTM G48-76 (reapproved 1980). Polytetrafluoroethylene cylinders, tied

together with the metal materials used in the experiment, were soaked in either a 5% NaCl solution or a solution with a different mixture of salts, kept at $92 \pm 1^\circ\text{C}$ for 72 hours and then removed, and their corrosion resistance was determined according to their contact boundary corrosion.

2. Experimental results and analysis

The changes of materials' energy of corrosion over time, i.e., the times when they reached stable energy of corrosion, are arranged in Chart 1. It can be seen that:



Key: (1). Anodized

Chart 1. Stability of energy of corrosion

(a) Aluminum alloys (sealed with hot deionized water): 1=water-sealed LY12CZ;

2=water-sealed 7075T76; 3=water-sealed LC4CS

(b) Titanium alloys (with anodized surfaces): 4=anodized TC1;

5= anodized TA7; 6=anodized TC4; ¹

(c) CFRM

(1) Compared with carbon fiber reinforced composite materials (CFRM), the energy of corrosion of the metallic materials was in a relatively negative position. When the materials were located in

¹ Although there is a number 7 in (b), there is no explanation of what material is represented by 7. Number 7 is probably 1Cr18Ni9Ti stainless steel, since it is one of the materials compared here, but it is not given a corresponding number on the chart.

a corrosion system, CFRM always stayed cathodic, while metal materials became positive and dissolved.

(2) From the $E_{\text{corr}}-t$ curve of the materials in Chart 1, one can see that over the course of 14 hours, the energy of corrosion of all the materials was fundamentally stable and unchanging. The greatest fluctuation value was at less than 0.02V. In addition, after being immersed in the solution, [materials' energy of corrosion] quickly became stable.

(3) The $E_{\text{corr}}-t$ curves of the materials in Statistical Chart 1 show that when the different materials' average E_{corr} (energy of corrosion) are arranged according to the materials' corrosion resistance, the order should be CFRM > anodized TA1 > anodized TA7 > anodized TC4 > 1Cr18Ni9Ti > TA1 > TA7 > TC4 > chromate-sealed LY12CZ > hot water-sealed LY12CZ > chromate-sealed 7075T76 > chromate-sealed LC4CS > hot water-sealed 7075T76 > hot water-sealed LC4CS. The chromate sealing mentioned here meant sealing aluminum alloys with chromate after first anodizing them; hot water sealing meant sealing aluminum alloys with hot deionized water after first anodizing them.

The changes over time in galvanic energy or galvanic current between different kinds of metals and CFRM or between metals and metals were relatively stable, as Charts 2 and 3 demonstrate. On the following page, comparison of a large quantity of firsthand experimental curves reveals:

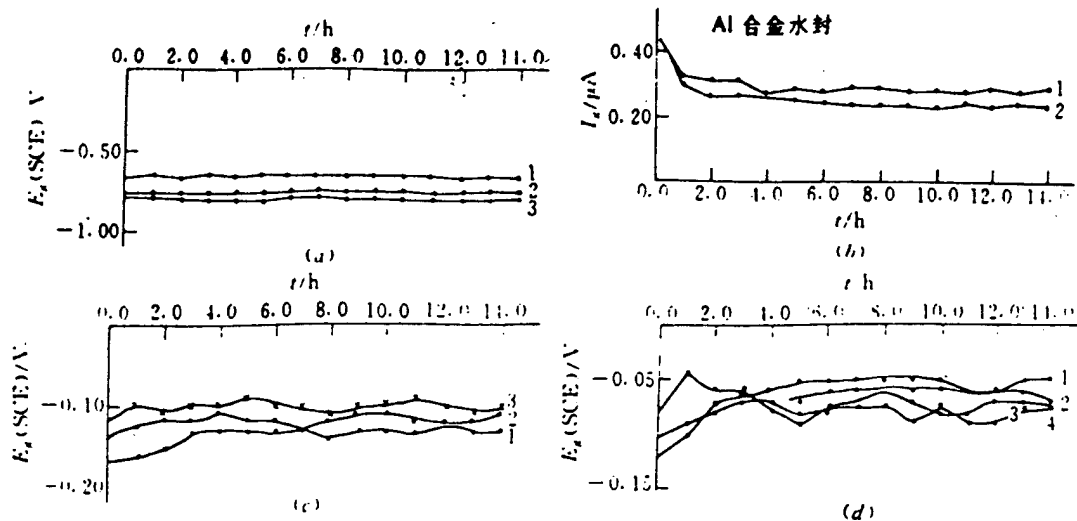


Chart 2. E_g - t correlation curves of CFRM coupled with other materials

(a) Aluminum alloys (sealed with deionized hot water): 1=LY12CZ/CFRM; 2=7075T76/CFRM (water-sealed); 3=LC4CS/CFRM (water-sealed)

(b) Aluminum alloys (sealed with deionized hot water): 1=7075T76/CFRM (water-sealed); 2=LY12CZ/CFRM (water-sealed); 3=LC4CS/CFRM (water-sealed)

(c) Titanium alloys (with non-anodized surfaces) and stainless steel (1Cr18Ni9Ti): 1=1Cr18Ni9Ti/CFRM; 2=non-anodized TC4/CFRM; 3=non-anodized TA1/CFRM

(d) Titanium alloys (with anodized surfaces): 1=anodized TA1/CFRM; 2=anodized TC1/CFRM; 3=anodized TA7/CFRM²

² A number 4 is given in chart (d), but no corresponding material is given for it.

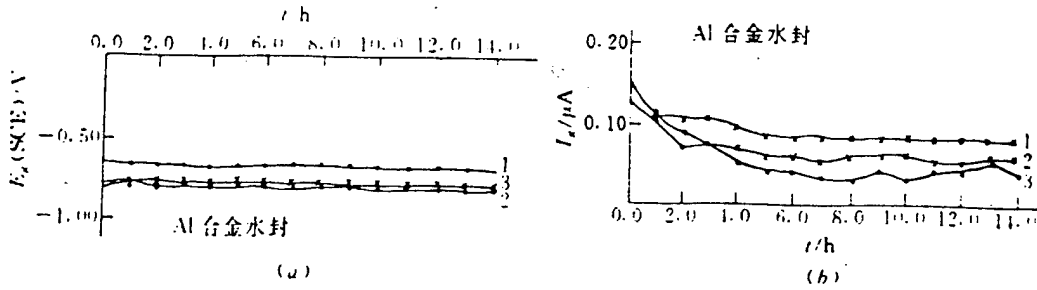


Chart 3 I_g - t correlation curves for aluminum alloys (sealed with hot deionized water) coupled with titanium alloys

(a) 1=LY12CZ/water-sealed TA1; 2=LC4CS/water-sealed TA1; 3=7075T76/water-sealed TA1

(b) 1=LC4CS/water-sealed TA1; 2=7075T76/water-sealed TA1; 3=LY12CZ/water-sealed TA1

(1) When carbon fiber reinforced composite materials are coupled with ionized titanium alloys, their average E_g value is close to 0.05V, and their average I_g value is less than $0.02\mu\text{A}/\text{cm}^2$. These were the stablest of the coupled materials in the study. On the contrary, hot water-sealed LC4CS/CFRM, chromate-sealed LC4CS/TA1, and hot water-sealed LC4CS/TA1 combinations had relatively high average E_g values (close to 0.8-0.9V) and average I_g values (close to $0.1\text{mA}/\text{cm}^2$). Their corrosion effect was thus stronger.

(2) From the I_g - t curve, one can see that although hot water-sealed 7075T76/CFRM, hot water-sealed LC4CS/CFRM, chromate-sealed 7075T76/CFRM, and chromate-sealed LC4CS/CFRM were couples of metals with highly corrosion-resistant carbon fiber reinforced composite materials, their galvanic current densities were higher than $0.2\sim 0.3\mu\text{A}/\text{cm}^2$. However, certain metal/metal couples had much lower galvanic current densities. For example, hot water-sealed LC4CS/TA1 and hot water-sealed 7075T76/TA1 couples' current density was approximately $0.05\mu\text{A}/\text{cm}^2$.

(3) An arrangement of the corrosion resistance of material couples according to their galvanic current density values is as follows: anodized titanium alloys/CFRM > non-anodized titanium alloys/CFRM > 1Cr18Ni9Ti/CFRM > aluminum alloys/CFRM. Metal/metal couples were

situated in between.

(4) If, after being anodized, aluminum alloys undergo a separate aftertreatment (either hot deionized water sealing or chromate sealing), their corrosion resistance can be improved. Experimental data on coupled materials are organized as shown in Table 1.

Table 1 Average I_g values and calculated i_g values of coupled materials

(1) 偶对材料	(2) 表面处理状态	I_g / mA	$i_g / \mu\text{A} \cdot \text{cm}^{-2}$
LY12CZ / CFRM	(3) 热水封闭	0.23	9.2
	(4) 铬酸盐封闭	0.21	8.4
LC4CS / CFRM	热水封闭	0.26	10.4
	铬酸盐封闭	0.22	8.8
7075T76 / CFRM	热水封闭	0.27	10.8
	铬酸盐封闭	0.24	9.6
LY12CZ / TA1	热水封闭	0.04	1.6
	铬酸盐封闭	0.03	1.2
LC4CS / TA1	热水封闭	0.18	3.2
	铬酸盐封闭	0.06	2.4
7075T76 / TA1	热水封闭	0.09	3.6
	铬酸盐封闭	0.06	2.4
LY12CZ / TC4	热水封闭	0.05	2.0
	铬酸盐封闭	0.04	1.6
LC4CS / TC4	热水封闭	0.07	2.8
	铬酸盐封闭	0.05	2.0
7075T76 / TC4	热水封闭	0.08	3.2
	铬酸盐封闭	0.05	2.0
TA1 / CFRM	-	0.76×10^{-3}	0.031
TC4 / CFRM	-	0.74×10^{-3}	0.030

Key: (1). Coupled materials. (2). Surface treatment. (3). Hot water-sealed. (4). Chromate-sealed

The United States Air Force's Flight Materials Laboratory (FML) stipulates that when experimenting with couples in a neutral aqueous solution, if $i_g < 5\mu\text{A}/\text{cm}^2$, then the metal material coupled with CFRM can be used "as is," such as a titanium alloy in Table 1. If $5\mu\text{A}/\text{cm}^2 < i_g < 15\mu\text{A}/\text{cm}^2$, the metal material coupled with CFRM can

be used, but it must undergo protective treatment beforehand. The i_g values of the aluminum alloys in Table 1 all fall within this range. It is especially clear from Table 1 that when anodized titanium alloys are coupled with CFRM, after two hours of stabilization, their i_g value is less than $0.004 \mu\text{A}/\text{cm}^2$, and they can effectively prevent galvanic corrosion. If, however, $i_g > 15 \mu\text{A}/\text{cm}^2$, the coupled materials cannot realistically be used.

The coupled samples were completely immersed in a 5% NaCl aqueous solution, one milliliter of H_2O_2 was added to every liter of solution, and the solution volume/sample area was kept at $> 20 \text{ml}/\text{cm}^2$. The pH was adjusted to 6, and [the materials] were kept soaking at $37 \pm 1^\circ\text{C}$ for 72 hours. The results of the soaking experiment are shown in Table 2 (see next page).

The [salt spray] experiment was carried out under conditions of continuous spraying. The saline solution was a 5% NaCl solution, adjusted to a pH level of 6-6.8, and kept at $35 \pm 1^\circ\text{C}$ for 168 hours. Corrosion ranks were determined according to the Soviet Union national standard (ГОСТ). Results of this experiment are also shown in Table 2.

Table 2 Results of the soaking corrosion and salt spray corrosion tests on coupled materials

(1) 试验材料	(2) 铝合金试样 表面处理状态	(3) 防护层材料	(4) 浸泡试验		(5) 盐雾试验	
			(6) 失重 / gm ⁻² · h ⁻¹	(7) 腐蚀 等级	失重 / gm ⁻² · h ⁻¹	腐蚀 等级
LY12CZ / CFRM	(8) 热水封闭	(10) 无	0.0284	5	0.0026	3
	(9) 铬酸盐封闭		<0.0003	1	<0.0003	1
LY12CZ / CFRM	热水封闭	(11) 聚氨酯清漆	0.0027	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
LC4CS / CFRM	热水封闭	无	0.0681	6	0.0048	4
	铬酸盐封闭		<0.0003	1	0.0006	2
LC4CS / CFRM	热水封闭	聚氨酯清漆	0.0030	3	<0.0003	1
	铬酸盐封闭		0.0007	2	<0.0003	1
7075T76 / CFRM	热水封闭	无	0.0546	6	0.0040	4
	铬酸盐封闭		<0.0003	1	0.0009	2
7075T76 / CFRM	热水封闭	聚氨酯清漆	0.0032	4	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
LY12CZ / TA1	热水封闭	无	0.0235	5	0.0029	3
	铬酸盐封闭		<0.0003	1	<0.0003	1
LY12CZ / TA1	热水封闭	聚氨酯清漆	0.0021	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
LC4CS / TA1	热水封闭	无	0.0544	6	0.0037	1
	铬酸盐封闭		0.0008	2	0.0011	2
LC4CS / TA1	热水封闭	聚氨酯清漆	0.0029	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
7075T76 / TA1	热水封闭	无	0.0436	6	0.0034	4
	铬酸盐封闭		<0.0003	1	0.0003	1
7075T76 / TA1	热水封闭	聚氨酯清漆	0.0027	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
LY12CZ / TC4	热水封闭	无	0.0268	5	0.0033	4
	铬酸盐封闭		<0.0003	1	<0.0003	1
LY12CZ / TC4	热水封闭	聚氨酯清漆	0.0024	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
LC4CS / TC4	热水封闭	无	0.0491	6	0.0044	4
	铬酸盐封闭		<0.0003	1	<0.0003	1
LC4CS / TC4	热水封闭	聚氨酯清漆	0.0027	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1
7075T76 / TC4	热水封闭	无	0.0474	6	0.0038	4
	铬酸盐封闭		<0.0003	1	<0.0003	1
7075T76 / TC4	热水封闭	聚氨酯清漆	0.0025	3	<0.0003	1
	铬酸盐封闭		<0.0003	1	<0.0003	1

Key: (1). Experimental materials (2). Aluminum alloy surface treatment (3). Protectant material (4). Soaking experiment (5). Salt spray experiment (6). Weight loss / gm⁻² · h⁻¹ (7). Corrosion grade (8). Hot water-sealed (9). Chromate-

[In the crevice corrosion experiment,] two different kinds of eroding agents, strong and weak, were used. The strong eroding agent was a 6% NaCl aqueous solution with a pH level of 5.5-6.5. The weak eroding agent was made up of 150 ml of a 6% FeCl₃ aqueous solution, to which was added 2g of NH₄Cl and 2ml of 36-38% concentrated hydrochloric acid. The temperature of both solutions was kept at 92±1°C continuously for 72 hours. Results of the experiment were as follows:

(1) The crevice corrosion samples of anodized aluminum alloy/CFRM couples that were treated with hot water sealing or chromate sealing demonstrated very strong crevice corrosion resistance in both kinds of solutions. Contact points on the surface of aluminum alloys only had a small amount of partial corrosion after soaking for 72 hours.

(2) After soaking the crevice corrosion sample of the 1Cr18Ni9Ti/CFRM couple in the weak erosion solution for 72 hours, slight pitting was discovered in the crevices; but severe crevice corrosion took place after the sample was placed in the strong erosion solution for 36 hours.

(3) After soaking in the weak erosion solution for 72 hours, no crevice corrosion took place in any titanium alloy/CFRM couples, no matter whether or not their surfaces were anodized. But after soaking in the strong erosion solution for 72 hours, they demonstrated very slight crevice corrosion. The order of crevice corrosion resistance of differently composed titanium alloys was TA1 > TA7 > TC4.

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³ Literally, this is *danbanji*, "single board machine." It was not found in any dictionary. *Danban jisuanji*, "single board computer," was the closest approximation.

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