

Bimetallic Compatibility for Space Applications

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Abstract: Experiments were undertaken to measure the extent of galvanic corrosion of materials combinations often used in the construction of a satellite under conditions encountered during manufacturing, testing and storage of the space hardware. A standard three-electrode technique was developed – working electrode, Pt counter electrode and SCE -, which was able to operate inside humidity-controlled atmosphere. This system has given appreciable results down to 60% RH. Polarization curves have been reported measured in 0.05% NaCl, 100% RH and 70% RH. The mixed potential theory is used to combine polarization curves of different materials and to obtain mixed potential and corrosion current for the bimetallic combinations. Using a threshold of $0.5\mu\text{A}/\text{cm}^2$ bimetallic corrosion tables can be constructed.

Keywords: bimetallic corrosion galvanic polarization potentiostatic

Introduction

In the construction of a satellite, two metals that form a compatible couple may have to be placed in electrical contact to one another to avoid charge build up. Requirements are often placed on the maximal electrical resistivity of this joint. Although this may not cause anomalies or malfunctions in the space environment, it has to be borne in mind that equipment on board the manned habitats of the International Space Station experience humidity levels are up to 70% RH and also that spacecraft and equipments often have to be stored on earth for considerable periods of time and that during storage they may inadvertently be exposed to environments where galvanic corrosion can take place and deteriorate the contacts.

Galvanic corrosion occurs when two dissimilar metallic materials exposed to a conductive medium (electrolyte) are electrically connected, as for instance in direct contact.

For galvanic corrosion to occur, three main conditions must be met:¹

- I. There must be a difference in electrochemical potential between the two metals – one serve as the anode and the other as the cathode
- II. There is a ionic path connecting the two electrodes
- III. There is an electrical path connecting the two electrodes

If any of these conditions are not satisfied, galvanic corrosion will not occur.

The less noble contact partner will corrode increasingly and is called anode, while the corrosion rate of the more noble material (cathode) will decrease. The nobility of a material is determined by the galvanic series for the electrolyte of interest: the less negative the potential is, the more noble it is. This means that the more negative the potential, the more active the material.

Bimetallic corrosion is a problem because it is usually localized and can occur very rapidly. In fact, this is known to have taken place on several occasions and it is for this reason that the European Space Agency has been studying the dangers involved.

Bimetallic corrosion as defined in this paper differs from the other forms of galvanic corrosion in that the anodic and cathodic sites of the corrosion cell reside separately on two coupled different metals (or conductive non-metal) comprising the corrosion cell, while all other forms of corrosion, the cathodes and anodes exist on the surface of the same metal.

When dissimilar metals are used in contact with each other and when they are exposed to an electrically conducting solution, then - as a general rule - combinations of metals should be chosen that are as close as possible in the galvanic series.

Coupling two metals widely separated in this series will normally lead to accelerated attack of the more active metal. These so-called electrochemical series can be found in many books and standards on galvanic corrosion.²⁻⁴

Table 1 - Galvanic series in Seawater

cathodic (noble)
Platinum
Gold
Graphite
Titanium
Silver
18-8 austenitic stainless steels (passive)
Iron-chromium alloys (passive)
Inconel (passive)
Nickel
Monel
Cupronickel alloys
Bronzes
Copper
Brasses
Tin
Lead
Cast iron
Mild steel and iron
Cadmium
Aluminium alloys
Zinc
Magnesium and alloys
anodic (active)

This well known series indicates the relative nobility of different metals and alloys in seawater, based on the measurement of corrosion potentials. In a galvanic cell, the more noble material in this series will become the cathode (no metal dissolution), while the less noble material will corrode as the anode. A greater separation of the materials in the galvanic series indicates a bigger potential difference between the materials; generally indicating a greater degree of galvanic incompatibility when coupled.

This galvanic series was derived for one specific electrolyte (seawater) only. The materials can have

different nobility ranking in different environments and at different temperatures.

The galvanic series are useful as a guide for metals to be joined. It will help the selection of metals having minimal tendency to interact galvanically. However, these tables cannot be used for determining the amount of corrosion between the members of the joint and also do not indicate the need or degree of protection to be applied to minimize this type of corrosion.

Often when design requires that dissimilar metals come in contact methods are developed to deal with these situations using the galvanic series and some engineering judgement. In many cases this is achieved by measuring the corrosion potentials in non-flowing water at room temperature containing 3.5% NaCl and applying rules for the maximum difference in potential depending on the environment. Simple rules were drawn up in the past to translate this difference to humidity conditions. A well-known rule was when this difference was less than 0,5 V, the combination of metals was save for use in clean room conditions and a maximum difference of 0.25 V was allowable when used under non-humidity and temperature controlled conditions. These result of these types of measurements and rules were also given in the ESA Q-70-71⁵. This easy rule is still in use in many places due to its simplicity and not because it is correct. There is no close relationship between the extend of galvanic corrosion under atmospheric conditions and the difference in corrosion potential measured in salt water. The simple rules as given here can be explained by a drastic simplification of the mixed potential theory, which lies at the basis of the bimetallic corrosion.

The relationship between the current and the voltage (the polarization curves) which describes the galvanic corrosion process of a metal is given by the Butler-Volmer equation given in equation 1, when the rate of reaction is controlled solely by the rate of the electrochemical charge transfer process, which is in turn an activation-controlled process.

Each metal and environment has its own constants for i_{corr} , α and z . When we combine two equations according to the mixed potential theory⁶ the intersection between the two equations determines the mixed potential and the corrosion current of this combination.

The simplification mentioned above is by making these constants the same for every metal and $\alpha=0.5$. In this case the corrosion current of every bimetallic couple is described by the difference in corrosion potential as shown in fig. 1 and a maximum allowable corrosion is translated into a maximum allowable voltage difference.

$$i = i_{corr} \left[\exp \left(\frac{\alpha z F}{RT} \eta \right) - \exp \left(\frac{-(1-\alpha) z F}{RT} \eta \right) \right] \quad \text{Eq.1}$$

i_{corr} : corrosion current

z : number of electrons; η : overpotential ($= E - E_{corr}$)

α : transfer coefficient, F : faraday constant

R : Gas constant, T : temperature

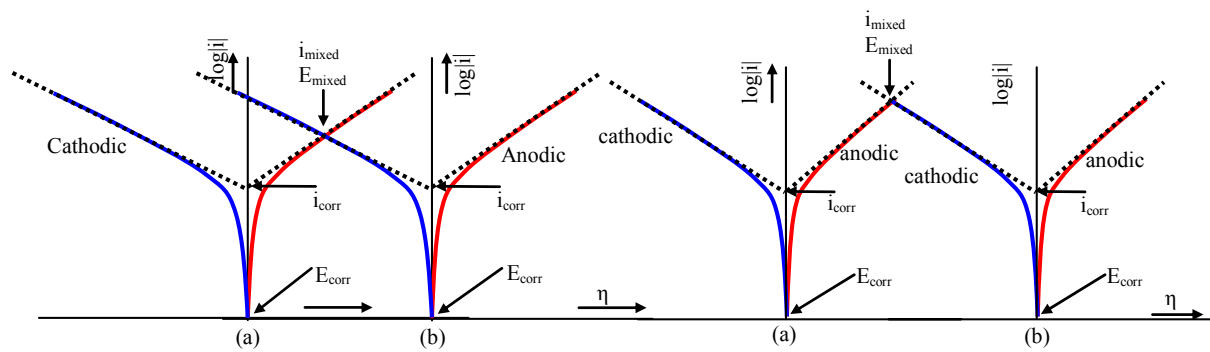


Fig. 1. Graphical presentation of the Butler-Volmer equation showing the result of increasing the corrosion current with larger EMF difference

Under certain circumstances these simplifications give a fair first idea if a combination shows an acceptable amount of bimetallic corrosion. In reality the general trend for the corrosion current i_{corr} is to become lower as the metal has a more positive corrosion potential (nobler metal). Also the oxygen process becomes more and more effective with thinning of the moisture layers,

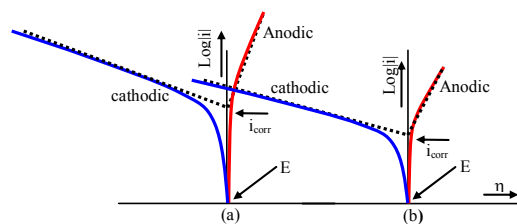


Fig. 2. Graphical presentation of a bimetallic couple having different constants

because the increased oxygen transport through these thin layers. This process cannot go on forever towards extremely thin absorbed moisture films encountered below 100% RH. Inhibition of the cathodic process can occur due to insufficient water present under these conditions. The anodic process will also be reduced as a result of the diminishing moisture layer, as a result of the appearance of anodic passivity. The passive state is strongly enhanced by the increased access of oxygen to the surface.⁷

These contributions will result in modified polarization curves as given in figure 2.

The cathodic part is now more horizontal and the major part of the bimetallic corrosion current (the crossing point of the cathodic part of the noble metal (a) with anodic part of the less noble metal (b)) is determined by the cathodic branch of the noble metal (b), while the mixed corrosion potential is close to the corrosion potential of the less noble metal (a). When the difference in corrosion potential changes, the current

follows the cathodic branch of the noble metal (b) and in extreme cases when this branch is horizontal due to minimal moisture layer on the surface can remain constant.

Following the above reasoning tests were defined for measuring the polarization curves under humidity conditions and combine them using the mixed potential theory. This has also the advantage over measuring using bimetallic couples that the number of samples is decreased dramatically. For example 100 metals make up 4950 combinations.

Experimental technique

The electrochemical tests were performed using an electrochemical workstation IM6e from Zahner-Elektrik. The I/E experiments were performed with a polarization rate of 2mV/s, starting always at the free corrosion potential E_{corr} and subsequently polarized anodically resp. cathodically.

Fig. 3. Sample for measuring single or bimetallic corrosion properties. CE: Counter Electrode; SCE: Saturated Calomel Electrode.

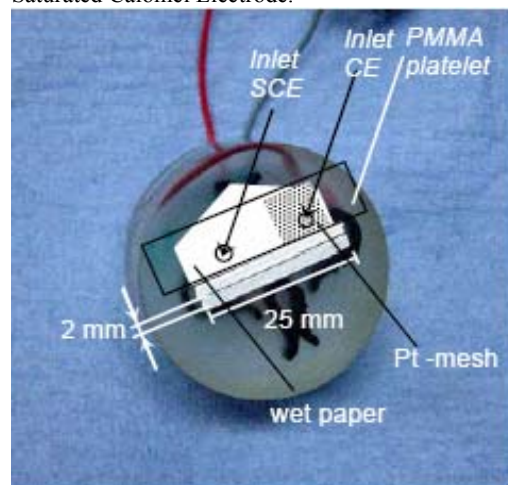


Table 2 -Composition information about the tested materials. GF: Goodfellow Cambridge Limited, Huntingdon, UK, ARM: Advent Research Material Limited, Eynsham-Oxford, UK.

	Symbol	Purity [%]	Composition	Thickness [mm]	Supplier
Carbon	C	99.5	-	2.5	GF
Titanium	Ti	99.6+	-	2.0	GF
Nickel	Ni	99.0+	-	2.0	GF
AA 7075 (Al-Zn-Mg-Cu)	-	-	Al 90/5.6Zn	2.0	Internal stock
Platinum wire	Pt	99.95	-	Ø 0.5	ARM
AISI 316	SS	-	Fe69/Cr18/Ni10/Mo3	1.0	GF
Magnesium	Mg	99.9	99.9	2.0	GF
Muscovite Mica	-	-	Potassium Aluminosilicate	0.025	GF

The experiments under immersion conditions were performed using the classical electrode arrangement in a 0.05% NaCl solution. This solution has a conductivity of approximately 1000 μ S/cm. Experiments under a humidity-controlled atmosphere were performed in a humidity chamber controlled by an automatic humidity controller provided with a humidity sensor. An ultrasonic humidification system, rotary vent vacuum pump and a laboratory gas-drying unit provided for the desired humidity level maintenance. A fan assured equal distribution of humidity overall the chamber volume. Humidity levels could be maintained with an accuracy of +/- 2 percent points of RH%.

Each sample was shortly before testing ground with 1200 grit paper and cleaned in an ultrasonic bath with ethanol.

A Pt electrode was used as counter electrode. In order to achieve a larger counter electrode surface area in contact with the electrolyte, a Pt mesh was positioned between the Pt-tip and the wet paper strip. A Saturated Calomel Electrode (SCE) was used as reference. A Pasteur pipette filled with KCl saturated agar-agar gel acted as salt-bridge connection between the SCE and the

sample surface. To avoid excessive leakage, a minuscule piece of Silly Putty was put at the pipette ending as a plug.

Samples

The materials to be investigated were mostly delivered in 2mm thick plates, which were then cut in pieces of 25x10 mm. The wires for electrical connection were connected using soldering or - for non-solderable materials - using conductive silver glue. Couples of different materials were then potted in Caldofix resin but kept separated by an electric insulating 25 μ m thick mica foil. After curing, the samples were mechanically ground with 1200 grit paper in order to expose the 25x2mm edges to the desired atmosphere. A sample layout is shown in figure 3.

Results and discussion

Potentiodynamic Polarization measurements

Figures 4-6 show average polarization curves for each of the 6 reported materials at 70% RH, 100% RH and their comparison with a polarization curve obtained in a 0.05% NaCl using standard procedures.

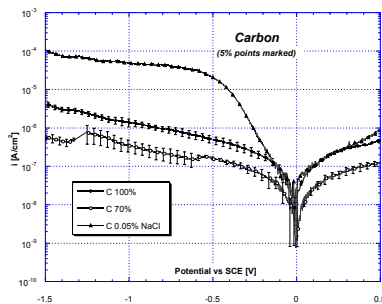


Fig. 4. Average polarization curves with standard deviation for Carbon.

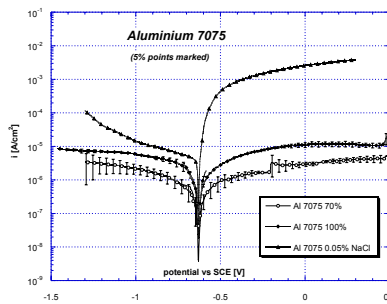


Fig. 5. Average polarization curves with standard deviation for AA7075.

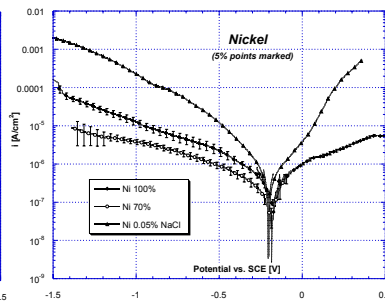


Fig. 6. Average polarization curves with standard deviation for Nickel.

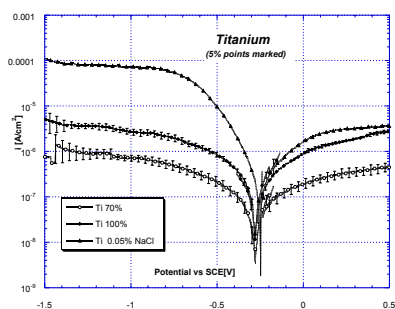


Fig. 7. Average polarization curves with standard deviation for Titanium.

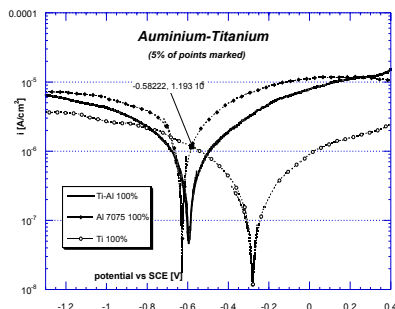


Fig. 8. Mixed potential theory compared with the direct experiment of the couple Al-Ti at 100% RH.

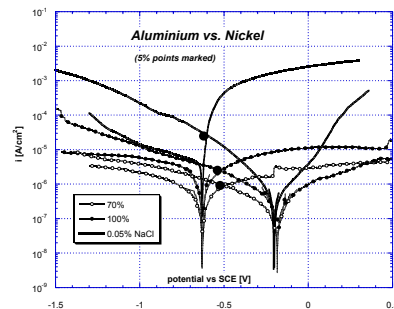


Fig. 9. Mixed potential theory applied to potentiodynamic curves of Al and Ni. Mixed potential becomes nobler with increasing humidity.

Figs.7-9 show average polarization curves for each of the four reported materials at 70% RH, 100% RH and their comparison with polarization curves obtained in a 0.05% NaCl using standard procedures. Additional materials such as Copper, Zinc and Tin-Lead were measured and included in the analysis but not displayed in the polarization graphs. The polarization curves in Figs. 4 to 7 are averages of several measurements. At each conductivity level at least three complete polarization curves are measured. The error bars in the plots depict the spread of the measured currents at the applied potential. The corrosion current is diminishing with decreasing humidity. In all investigated metals the same trend can be observed. The corrosion current I_{corr} (calculated from the polarization curves) is decreasing with decreasing humidity.

Comparison of data at 100% RH given in Fig. 8 between direct measurements on the Al-Ti combination and using the mixed potential theory when combining the individual Al and Ti results shows that both methods reveal very similar results. The observation that the corrosion current is changing in one direction when lowering the humidity is also true for the mixed potential. As illustrated in Fig. 9 the combination of Aluminium vs. Nickel and using the mixed potential theory shows that the mixed potential becomes nobler with decreasing humidity. In all cases the mixed potential of metal combinations is close to the corrosion potential of the anodic member. The lower corrosion current of the cathodic member (nobler) of the combination and the shape of the cathodic curve of the nobler metal following the hindering of the cathodic depolarization as explained in the beginning of this section, explains why this type corrosion under the circumstances given are cathodically controlled. This means with material combinations having the same cathodic member, the mixed properties can be estimated from relative position of the corrosion potential of the anode in relation to the cathode. Electrochemical

impedance measurements were reported during the 16ICC⁸.

Classification

The requirement to obtain a certain classification could for instance be that the measured corrosion current should not pass a certain threshold below 70% RH. The decision of the critical galvanic current density value is very arbitrary and requires experience such as the

Table 3 - Correlation between corrosion rate and level of corrosion according to NAE

Resistivity [kΩ.cm]	i_{mixed} values [μA/cm²]	Corrosion
> 100	< 0.1	Negligible
50 - 100	0.1 - 0.5	Low
10 - 50	0.5 - 1	Moderate
<10	1	High

knowledge of the galvanic corrosion behaviour for certain galvanic couples as a reference. As an example, for the safety of nuclear installations, the Nuclear Energy Agency, NEA, assess the level of corrosion – mainly in concrete - according to Table 3⁹. But other authors give different relationships between the corrosion currents and the corrosion severity.

Table 4 - Correlation between corrosion rate and corrosion severity according to K. Clear

i_{mixed} [μA/cm²]	Corrosion rate [μm/year]	Corrosion severity
<0.5	6	No corrosion damage expected
0.5-2.7	6-30	Corrosion damage possible in 10-15 years
2.7-27	3-300	Corrosion damage expected in 2-10 years
>27	>300	Corrosion damage expected in 2 years or less.

K. Clear¹⁰ for the corrosion of steel in field concrete structures sets $0.5\mu\text{A}/\text{cm}^2$ as a limiting corrosion current – see Table 4

We could attribute to every ECSS class as presented in

Table 5 - Assessment of galvanic couples in this study

	ECSS classes	In this study
0	can be used without restrictions	In wet conditions
1	can be used in a non-controlled environment (doesn't require a clean room)	In all dry conditions (less or equal to 100% RH)
2	can be used in clean room	Possible to use in manned spacecraft (maximum 70%RH)
3	needs specific measures to avoid galvanic corrosion	Critical (not possible to use even at 70 % RH)

ECSS-Q-70-71 the corrosion current limits reported by NAE in table 3 and obtain a classification for a single environment (e. g. for 70% RH environment).

To make a general classification we can consider one critical current under which, the galvanic combination is considered safe to use. As a first approximation we take as upper limiting current value $0.5\mu\text{A}/\text{cm}^2$ - according

Table 6 - The couples with a corrosion current lower than $0.5\mu\text{A}/\text{cm}^2$ in 0.05% NaCl are in the first safest class: class 0

0.05% NaCl	Mg	Zn	Al 7075	Fe	Ti	Ni	Cu	Aisi316	C
Mg		110	130	240	87	390	200	200	73
Zn			10	68	68	96	60	44	44
Al 7075				33	27	27	29	34	32
Fe					4.3	6.2	4.5	9.1	10
Ti	0					0.21	0.31	0.42	0.32
Ni	1,2 or 3						0.22	0.38	0.25
Cu								0.46	0.04
Aisi316									0.10
C									

Table 8 - The additional couples with a corrosion current lower than $0.5\mu\text{A}/\text{cm}^2$ at 70% RH is in the third safest class: class 2 and the remaining in the most critical class: class 3

70% RH	Mg	Zn	Al 7075	Fe	Ti	Ni	Cu	Aisi316	C
Mg		0.63	1	0.26	0.89	1.15	1	0.89	0.51
Zn			1	0.27	0.61	1.5	1	0.78	0.27
Al 7075				0.19	0.3	0.92	0.96	0.54	0.16
Fe					0.14	0.49	0.68	0.4	0.13
Ti	0					0.064	0.075	0.097	0.064
Ni	1						0.037	0.097	0.05
Cu	2							0.096	0.05
Aisi316	3								0.04
C									

to NAE in table 3.

The obtained general classification is reported Table4.

The results of for the mixed corrosion current as determined by the mixed potential theory are given in tables 5 to 7

We will set first all combinations tested in 0.05% NaCl solution and having a corrosion current of $<0.5\mu\text{A}/\text{cm}^2$ to class 0 meaning that these combination can be used under all conditions. The results are displayed in table 5.

As second we will now set all combinations tested under 100% humidity and having a corrosion current of $<0.5\mu\text{A}/\text{cm}^2$ to class 1 (leaving the previous assessed untouched) meaning that these combination can be used in a non-controlled atmosphere. The results are displayed in table 6.

The last action is to set all combinations tested under 70% humidity and having a corrosion current of $<0.5\mu\text{A}/\text{cm}^2$ to class 2 (leaving the previous assessed untouched) meaning that these combination can be used in a controlled atmosphere such as manned space or cleanrooms. The remaining combinations will be set to class 3, meaning that these combinations are critical and

Table 7 - The couples with a corrosion current lower than $0.5\mu\text{A}/\text{cm}^2$ in at maximum humidity of 100% RH are in the second safest class: class 1

100% RH	Mg	Zn	Al 7075	Fe	Ti	Ni	Cu	Aisi316	C
Mg		4.5	6	4.9	3.6	9	2.9	5.9	2.9
Zn			4	4	2.3	6.2	2.7	6.2	1.1
Al 7075				1.8	1.2	2.4	2.1	3.4	0.63
Fe					0.49	1.1	1.4	2	0.42
Ti	0					0.2	0.24	0.35	0.19
Ni	1						0.02	0.19	0.14
Cu	2 or 3							0.28	0.15
Aisi316									0.11
C									

should be avoided or protective measures should be taken. The results are displayed in table 7

Table 8 summarizes table 5, 6 and 7. This table shows a very good resemblance with the bimetallic corrosion table as found in ECSS-Q-70-71 for the metals displayed.

Conclusion

A relative easy classical three electrode configuration adaptation for polarization experiments in not immersed environments has been successfully developed and subsequently tested performing potentiodynamic polarization experiments on Al, Ti, Ni, SS, Mg and Carbon in a humidity chamber at different humidity levels. The system has given appreciable results down

to 60% RH and the adopted electrode configuration gave comparable results to test performed with the standard arrangement advised by the American Society for Testing and Materials, which is however only possible to use in immersion.¹¹

The developed method permits the acquisition of quantitative information directly in the environment of interest and to considerably reduce the amount of experiments necessary to define the mixed corrosion properties. Once a polarization curve for a material is determined, it is possible to combine it with every other material without the need of producing a specific bimetallic sample. For qualitative prediction of galvanic corrosion behaviour of not measured combinations, corrosion rates can even be estimated by assuming that the polarization curve must be included between already measured curves of two other similar materials sitting at the left and at the right side in the galvanic series.

The data displayed in table 8 shows that this method is capable of producing reliable figures for the bimetallic couples involved. It depends of course on the threshold set at $0.5\mu\text{A}/\text{cm}^2$. This value needs to be investigated in more detail.

An improvement foreseen for the future is the replacement of the standard reference electrode by a contactless reference one, such as a Kelvin Probe connected to a potentiostat using a smaller working electrode surrounded by a circular counter electrode.¹²

Acknowledgements

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