POLARIZATION MEASUREMENTS UNDER ATMOSPHERIC CONDITIONS USING A KELVIN PROBE AS A REFERENCE ELECTRODE

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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 three electrode system was used where a Kelvin probe acted as a reference electrode. The relation between potentials measured with the Kelvin probe system and the standard three electrode system using a calomel electrode was established under 70% and 90% RH. The polarization curves of Al, Ni and Ti were measured under 70% and 90% RH. The mixed potential theory is used to combine polarization curves of the different materials and to obtain mixed potential and corrosion current for the bimetallic combinations.

Keywords: Bimetallic Corrosion Galvanic Polarization Atmospheric Humidity Kelvin Probe

INTRODUCTION

In the construction of a satellite, two metals may have to be placed in electrical contact with one another to avoid charge build up. The metallic joints in satellite systems are usually part of an electrical grounding circuit. To avoid charge build up, the requirements on these joints are typically 2.5-7.5 mΩ. To guarantee this, a careful selection is made on the material combinations, so that bimetallic corrosion is minimised.
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 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. 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.

The assessment of the galvanic compatibility under atmospheric conditions between two dissimilar metals is currently based on the difference of their corrosion potentials measured in 3.5% NaCl water solution. 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 0.5V, the combination of metals was safe for use in clean room conditions[1]. 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 extent of galvanic corrosion under atmospheric conditions and the difference in corrosion potential measured in salt water.

In the European series of Space Standards the ECSS-ST-Q-70-71 [2] refers to the data selection of materials and contains a bimetallic compatibility table. The rules used for producing this table is given table I. An abstract from this table only showing the materials from this study is given in table 2. This table is derived using differences in corrosion potential of the two members of the couple taking into account the results from in house studies presented in [1].

Table 1: 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 90-100% 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)

Table 2: Abstract from ECSS-ST-Q-70-71A

	Pure metals and alloys in alphabetical order	B	K	Q
B	Al (pure) Al-Zinc alloys		3	3
K	Nickel, Monel, Inconel Nickel/Molybdenum-alloys			1
Q	Titanium & Ti-alloys			

An attempt was made to measure the polarization curves under more realistic conditions. Tests were performed under 70% and 100%RH conditions using a standard three electrode configuration. These results were presented during the 16th ICC in Beijng.[3]

We could attribute to every ECSS class as presented in ECSS-ST-Q-70-71 the corrosion current limits reported by NEA in [4] 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 μA/cm^2 - according to [4]

The results of this classification were presented in [5] where it was shown that method gave comparable results as found in [2]
The disadvantage of using a three electrode system is that the reference electrode is more or less in contact with the counter and working electrode, although via a very thin water layer. This might influence the local environment around the working electrode; also the thin water layer might dry-out during the measurements especially at low humidity levels.

In the present investigation the reference electrode is replaced by a Kelvin probe. The Kelvin probe together with the sample is placed inside a humidity controlled chamber.

TEST SETUP

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%. See figure 1.
The test temperature was 25°C.

The Kelvin probe type KP030S from KP Technology-Scotland uses a 1mm diameter gold plated tip
The complete Kelvin probe was placed inside the humidity chamber. To prevent short circuits in the Kelvin probe, a local humidity chamber was constructed around the vibrating head, keeping this part at humidity levels of around 70%RH max. See figure 2.

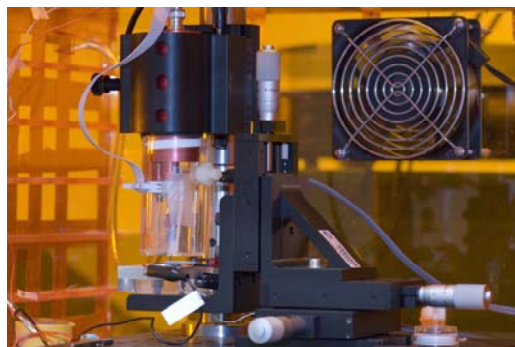**Figure 1: Kelvin probe inside humidity chamber**

Figure 2:Local humidity chamber around Kelvin probe head

The output of the Kelvin probe was connected to a conventional potentiostat. With the present setup it was not possible to run the experiments is the potentiostatic mode, while it was not possible to control the voltage of the Kelvin probe using an external potentiostat. The Kelvin probe setup was used in a galvanic mode with a programmable current. The electrochemical tests were performed using an electrochemical workstation IM6e from Zahner-Elektrik.

Sample layout

The materials to be investigated were delivered in 2mm thick plates, which were then cut in pieces of 25x10 mm, with composition as shown in table 3.

Table 3: Composition information about the tested materials by Goodfellow Cambridge Limited, Huntingdon, UK,

	Composition	thickness
Aluminium	99.99	2
Titanium	99.0+	2
Nickel	99.6+	2

A parylene coating of 5 μm was applied to the working electrode. An adhesive kapton tape of 25 μm thickness is attached to both sides of the working electrode. The two stainless steel counter electrodes of 20x10x1mm are mounted at both sides so that a cap of 30-35 μm exists between the working electrode and the two counter electrodes. A hole is drilled in the electrodes and wires are connected via the drilled holes to the working and counter electrodes by soldering or conductive silver paste.

This configuration is mounted in a clear cold setting epoxy resin. This microsection is ground and polished down to 1 μm using standard techniques. The electrodes are checked for short circuits and the cap between the working electrodes and the counter electrodes is checked that is shall not exceed 35 μm of distance.
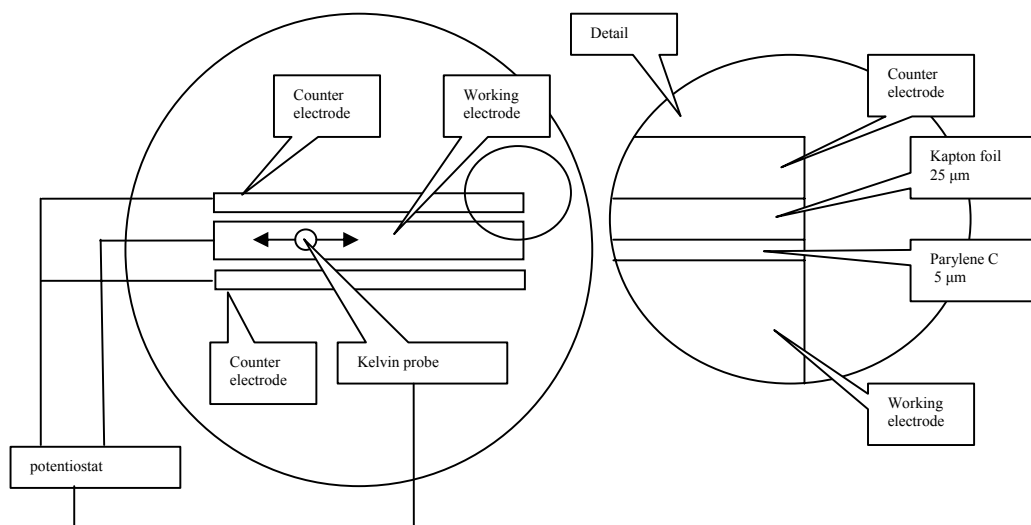

Figure 3: sample layout and connections

Each sample was shortly before testing ground with 4000 grit paper and cleaned in an ultrasonic bath with ethanol.

For electrochemical experiments under humidity conditions, specimens required some additional preparations: A hydrophilisation of the surface was necessary to assure an equally thick electrolyte film across the sample. This was achieved by means of a plasma treatment on air leak during approximately 10 s using a Plasmod of Tegal Corporation. Spreading 75μl of a 0.5% NaCl solution on the sample surface; this corresponds to a 60μm water layer with a conductivity of 10mS/cm. The sample was transported to the humidity chamber leaving it to dry it out at 50% RH level to activate the surface. Hereafter the humidity level was increased to the required level for testing.

RESULTS AND DISCUSSION

Comparison SCE and KP

The relation between the potentials measured with the Kelvin probe system and the standard Calomel system was established using an available set of materials with galvanic potentials ranging from +150mV to -1500mV. The standard calomel method used a micro salt bridge for contact to the sample surface. These materials (Mg, Al, Zn, Be, Fe, Pb, W, Cu, Ti, Monel400, Ni, Aisi304, Ag, Au and C – in plate form) were ground and polished using standard procedures down to 1 μm, plasma cleaned as described in the sample preparation, activated and measured. The measurements were performed at 70% and 95% RH until stabilization of the potential. Each material is tested five in different locations.
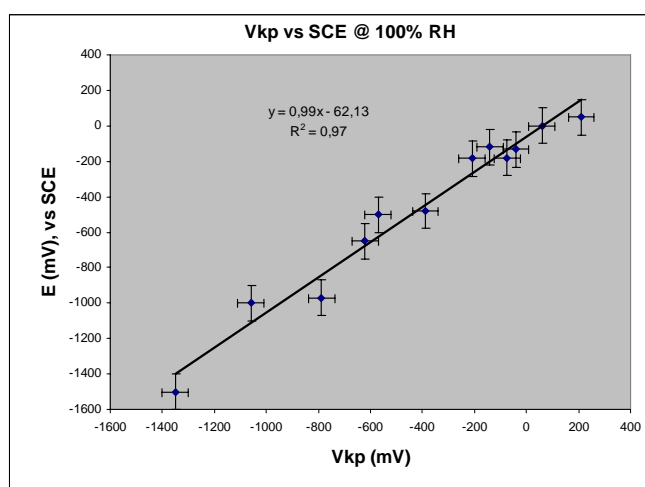

Figure 4: Relation between Kelvin probe potential and potential measured with a SCE at 100% RH
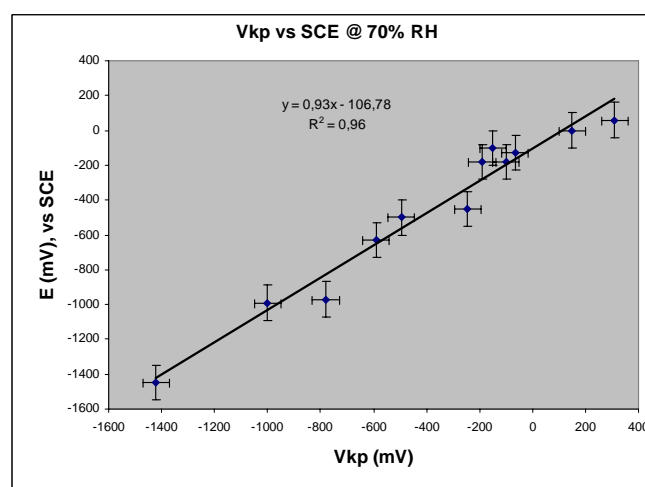

Figure 5: Relation between Kelvin probe potential and potential measured with a SCE at 70% RH

The relation between the potential measured with the Kelvin probe and using a saturated Calomel electrode is seen as a straight line as predicted by Stratmann and Streckel[6] with a slope is very close to 1 under both conditions as expected. The value of the constant is depends on the work function of the Kelvin probe tip under the given environmental conditions.

The value of the potentials of the individual metals depends also on the plasma cleaning treatment. Although this is taken as short as possible, its influence can noticed with the least noble metals such as Mg, Zn and to a lesser extend Al. The potentials of these metals is shifted to a more positive value due to the existence an oxide layer after the plasma cleaning process. Overall this does not change the slope and offset significantly.

Galvanic polarization

The stabilization of the potential after a current change takes some time. The polarization rate was set to 1nA/s, which is the slowest speed possible on the used potentiostat. In order to investigate to the dependence of the I/E curves on the polarization rate using the Kelvin probe, special scripts were written to slow down the polarization rate to 10pA/s. Small difference were found as seen in Fig. 6. These

differences were smaller than the standard deviation of the results following several repeated measurements.
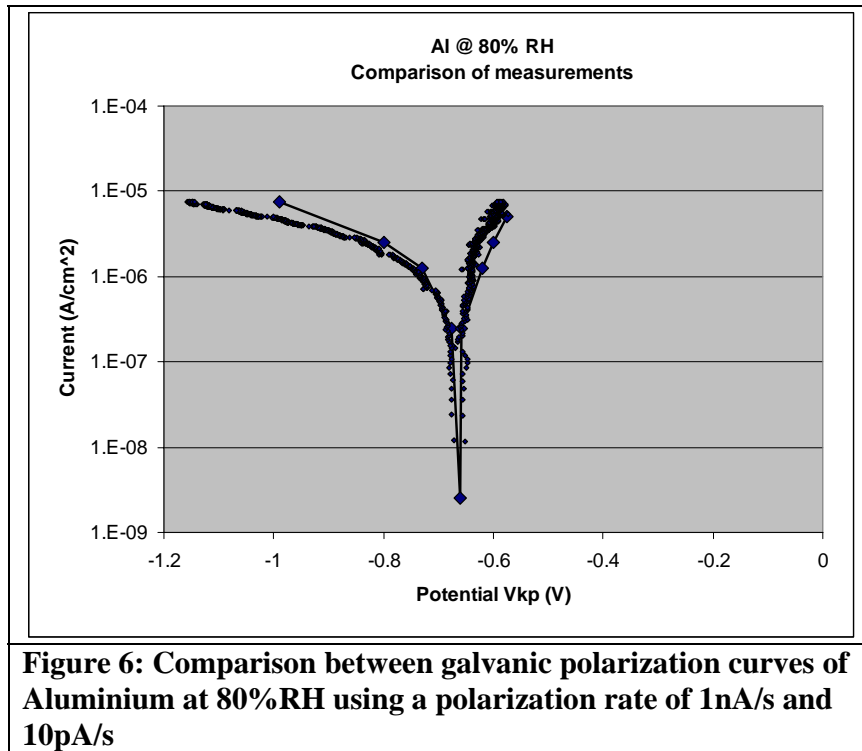

Figure 6: Comparison between galvanic polarization curves of Aluminium at 80%RH using a polarization rate of 1nA/s and 10pA/s

Aluminium, Nickel and Titanium are measured separately. Aluminium and Titanium is measured with a polarization rate of 1nA/s, while Nickel is measured with a polarization rate of 10pA/s. Figs. 6-8 show average polarization curves for each of the three reported materials at 70% RH and 90% RH. The polarization curves are averages of several measurements. At least three complete polarization curves are measured at each humidity level.
The results on the corrosion potential and corrosion current are given in table 3.

Table 2: Corrosion potential and corrosion currents of Al, Ti and Ni at 70 and 90% RH

	70% RH		90% RH	
	E_{corr}	I_{corr}	E_{corr}	I_{corr}
Aluminium	-0.66	0.1	-0.66	0.7
Titanium	-0.12	0.07	-0.12	0.08
Nickel	-0.17	0.03	-0.17	0.04

The mixed potential and mixed corrosion currents are established using the mixed potential theory.[7] The Aluminium and Nickel polarization curves are combined in fig. 7. The intersections of the anodic part of the Nickel curves and the cathodic parts of the aluminum curves gives us the mixed corrosion potential and mixed corrosion current of the Al-Ni couple. The results are given in table 4.
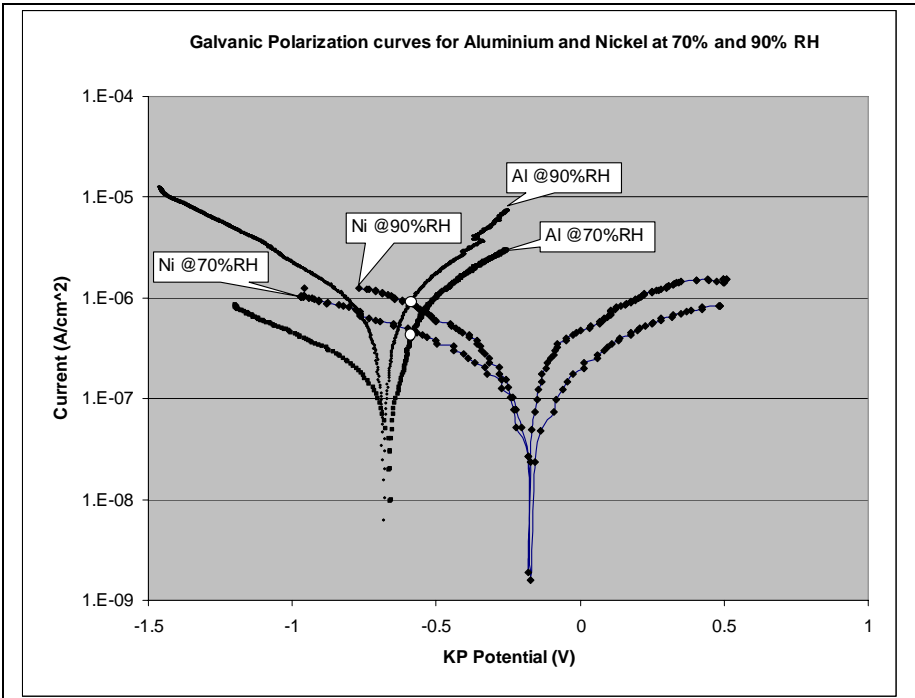
Figure 7: Mixed potential theory applied to potentiostatic curves of Al and Ni. Mixed values indicated by dot.

Table 3: Mixed potential and mixed corrosion current for the Al-Ni couple

	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)
70% RH	-0.57	0.46
90% RH	-0.58	0.9

The Titanium and Nickel polarization curves are combined in fig. 8. The intersections of the anodic part of the Nickel curves and the cathodic parts of the aluminum curves gives us the mixed corrosion potential and mixed corrosion current of the Ti-Ni couple. The results are given in table 5.
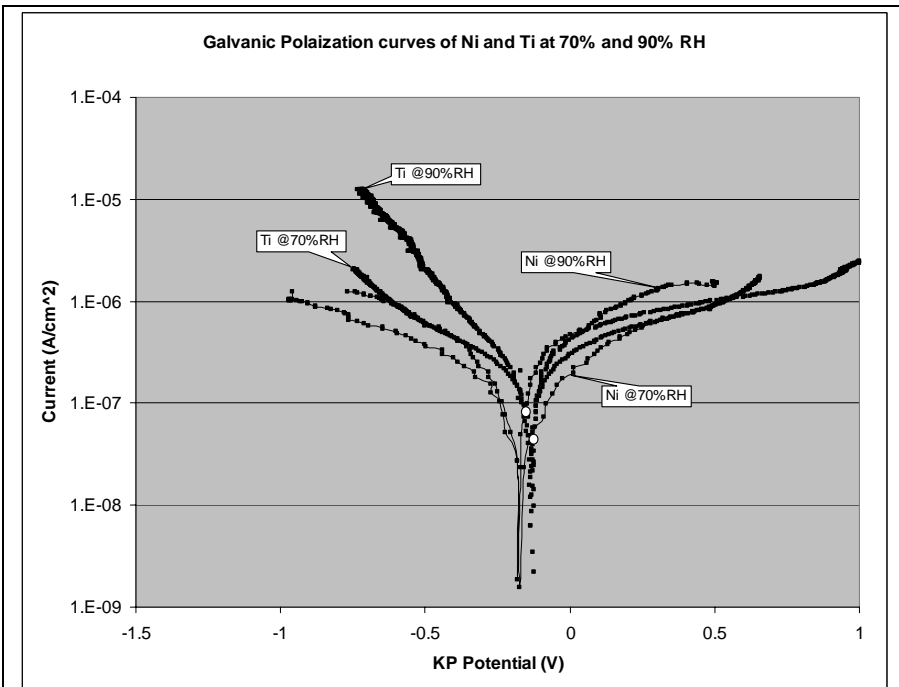

Figure 8: Mixed potential theory applied to potentiostatic curves of Ti and Ni. Mixed values indicated by dot.

Table 4: Mixed potential and mixed corrosion current for the Ti-Ni couple

	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)
70% RH	-0.14	0.05
90% RH	-0.16	0.07

The Aluminium and Titanium polarization curves are combined in fig. 9. The intersections of the anodic part of the Nickel curves and the cathodic parts of the aluminum curves gives us the mixed corrosion potential and mixed corrosion current of the Al-Ti couple. The results are given in table 6.
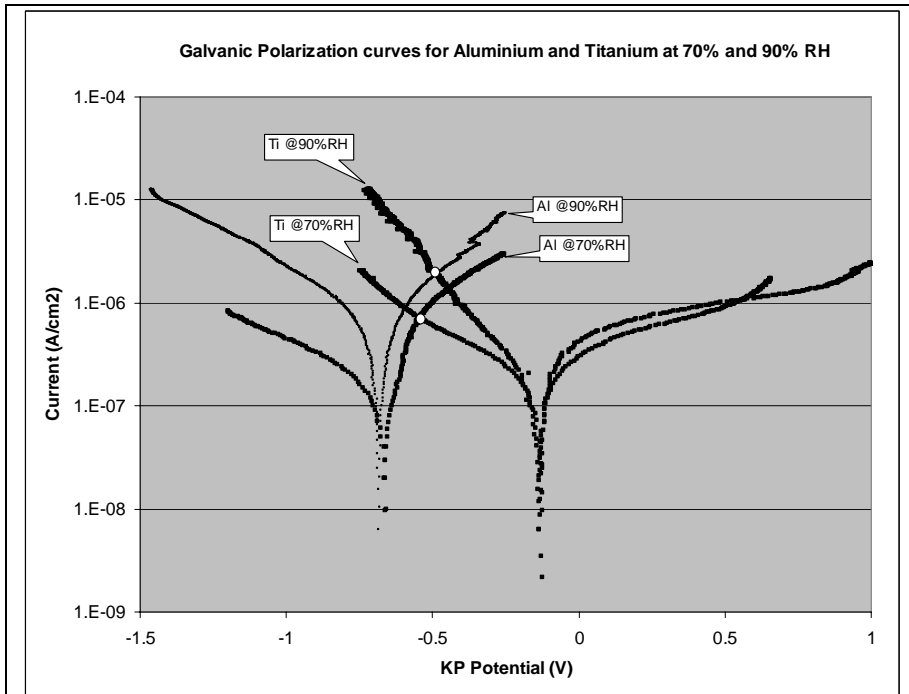

Figure 9: Mixed potential theory applied to potentiostatic curves of Al and Ti. Mixed values indicated by dot.

Table 6: Mixed potential and mixed corrosion current for the Al-Ti couple

	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)
70% RH	-0.56	0.75
90% RH	-0.50	2.0

DISCUSSION

The corrosion current is diminishing with decreasing humidity. The oxygen depolarization process becomes more and more effective with thinning of the moisture layers, because of the increased oxygen transport through these thin layers. This process cannot go on forever towards extremely thin absorbed moisture films encountered below 100% RH. Hindering of the cathodic depolarization 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, the result being the appearance of anodic passivity. The passive state is strongly enhanced by the increased access of oxygen to the surface.

The corrosion current is calculated per unit area. This means that the surface are of the working electrode must known. To avoid that the area in the gap between the working electrode and the kapton foil is acting as a part of the working electrode, due to ingress of moisture because of lack of edge retention, the sides of the working electrode were coated with Parylene C. This worked out to be a success, while no electrolyte was seeping out of gap between the two electrodes.

The sample layout with a counter electrode at both sides of the working electrode also diminishes the possible transmission line behaviour at low humidity levels. This TML behaviour might reduce the effective surface of the working electrode.

Using the rules given in table 1 and the save corrosion current as given in [4] of 0.5 µA/cm2, we arrive at a classification as displayed in table 7.

Table 7: Bimetallic compatibility results using to table 1

	Metals and alloys in test	B	K	Q
B	Al (pure)	■	2	3
K	Nickel (pure)		■	1
Q	Titanium (pure)			■

Comparison between table 2 and table 7 shows that in this study the Al-Ni couple is rated less corrosion susceptible than as given in ECSS-ST-Q-70-71A. In this standard the bimetallic compatibility between Aluminium and Nickel was calculated by the difference corrosion potential measured in 3.5% NaCl water solution. In this solution the potentials of Al and Ni are respectively -0.75V and -0.18V giving a delta of 0.57V, which is translated in ECSS-ST-Q-70-71 as being a high risk and labeled as 3.

CONCLUSION

The mixed potential theory could be confirmed as applicable also in humidity-controlled atmospheres. The corrosion behaviour under atmosphere conditions using a Kelvin Probe was found generally in line with the one obtained using a saturated calomel electrode configuration. The SCE configuration showed lower corrosion currents at the anodic and cathodic parts due to a drying-out of the water layer between the sample and the reference electrode of the after long measuring times. This is not the case for the Kelvin probe configuration. This resulted in slightly higher corrosion current than presented in [2]. The results have shown that the present configuration is a promising for measuring the corrosion currents and corrosion potentials without interference to the surface.

FUTURE OUTLOOK

A study is undertaken together with KP Technology to improve the way the Kelvin probe is used for corrosion studies. A dual tip head with individually controlled tip for faster scan measurements is being investigated.
Electrical Impedance Spectroscopic (EIS) measurements could be performed by modification of the electronics and by injecting an AC sine wave.

ACKNOWLEDGEMENTS

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