ALUMINUM AND SULFUR IMPURITIES IN ELECTROPOLISHING BATHS*

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Abstract

This study highlights the impurities formation in Electropolishing bath (mixture of sulfuric and hydrofluoric acids) when aluminum is chosen as cathode material. Such impurities could partially explain the performance disparities observed on electro polished niobium RF cavities.

These products might be aluminum derivatives, sulfur S and hydrogen sulfide H_2S.

Furthermore, parameters such as temperature, acid concentrations are also taken into account with or without applied voltage.

INTRODUCTION

There are several electropolishing (EP) processes applicable to niobium [1], but the mot efficient one was developed by Siemens in the 70's [2], in a mixture of sulfuric and fluorhydric acids. It is easily applied on small area, but as it consists of alternative steps of polishing, which stops with the growth of an oxide layer, followed by a stirring step in order to dissolve this insulating layer, it is more difficult applying it on large scale. A pioneering work has been done at KEK [3] to develop a large scale set-up, applicable to big cavities with a fairly good reproducibility. They proposed in particular a continuous process, were the continuous supply of electrolyte via a circulation system prevents the formation of the insulating layer. They also studied all the practical aspect of the problem (e.g. the resistance of various polymers to the etching mixture) and were the first to point out aging of the solution and sulfur generation. They also claim that aluminum, chosen for the cathode, is passive in the etching mixture. They are now some evidence that some corrosion is somewhat occurring, and we have tried to specify in what conditions.

Results on EP cavity treatment exhibit large discrepancies in performance, and they are some indications that they are more sensitive to field emission [4]. Sulfur particles produced during the EP process are possible candidates responsible for field emission. S production and Al corrosion were also observed in other labs (see e.g. [5]).

The aim of this study is do analyze and quantify impurities generation in EP bathes coming from the aluminum cathode or from the sulfuric acid. Two cases will be considered: with or without applied voltage in the cell.

ALUMINUM IN MINERAL ACIDS: STATE OF THE ART

The corrosion of aluminum has been widely studied; see e.g. [6-10]. It is largely connected with the behavior of its surface oxide and its amphoteric character. Dissolution of aluminum occurs readily in strong, non oxidizing acids and bases. In neutral or weakly acidic solution, Al is quite resistant to corrosion [8].

The apparent passivity of aluminum in the EP solution comes from the particularity of fluorinated salts formed in presence of HF, as will be seen hereafter.

Alumina and acids

Alumina Al_2O_3 forms on Aluminum surface in wet atmosphere or water and is approximately a 4-9 nm layer which is well adhering and impermeable to water and oxygen. Its exact composition may be very complex and varies a lot with environmental conditions, so it is often recommended to "regenerate" by etching in e.g. nitric acid before any surface treatment [6].

Note: as this layer is dissolved by mineral acids. Small quantities of this product will be irremediably introduced in the EP bath each time the aluminum cathode is plunged into the EP bath and will also be a source Al in the bath.

Aluminum and hydrofluoric acid

Aluminum is heavily corroded in usual aqueous (40-50 % HF), but this corrosion seems to be inhibited in anhydrous acid (80-99%) [6, 8]. This is due to the fact that the reaction product AlF_3 is hardly soluble in anhydrous media.

$$2\,Al + 6\,HF = 2\,AlF_3 + 3\,H_2 \qquad (1)$$
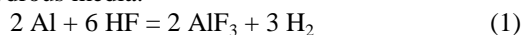
This property has been used to prevent aluminum dissolution in e.g. nitric acid [6]. We can infer that the same mechanism applies in HF- H_2SO_4 mixture.

By the way, if the water fraction becomes more important, the corrosion of Al starts again, as it can be observed on Figure 2 (next §).
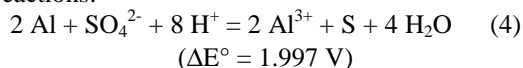
Aluminum and sulfuric acid

Diluted and cold, H_2SO_4 slowly attacks aluminum according to the reaction:

$$2\,Al + 6\,H^+ = 2\,Al^{3+} + 3\,H_2 \qquad (2)$$
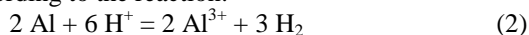
If we introduce sulfates in the balance, it comes:

$$2\,Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3\,H_2 \qquad (3)$$

Furthermore, some reactive metals can reduce H_2SO_4 into S and even H_2S when it is hot and concentrated [11]. Aluminum is very electronegative. Thus, we might expect the reactions:

$$2\,Al + SO_4^{2-} + 8\,H^+ = 2\,Al^{3+} + S + 4\,H_2O \qquad (4)$$
$$(\Delta E° = 1.997\ V)$$
$$2\,Al + 3\,S + 6\,H^+ = 2\,Al^{3+} + 3\,H_2S \qquad (5)$$

(ΔE° = 1.806 V)

In oxiacids (HNO_3, H_2SO_4) at high concentration the oxidizing effect prevails, and passivity is again observed [6, 8].

The next paragraph describes the experimental observations that confirm and precise the condition of sulfur and H_2S generation.

CORROSION OF Al WITHOUT APPLIED VOLTAGE

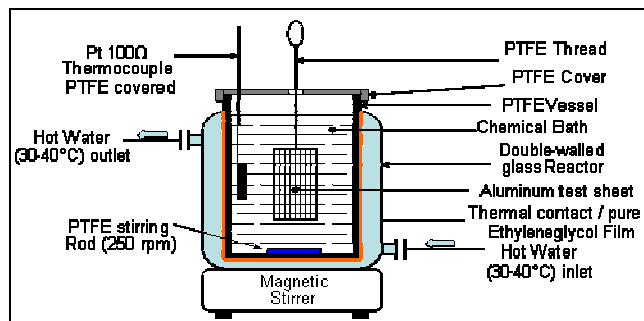## Experimental protocol

Figure 1: Scheme of Experimental Setting.

Al samples undergo the following procedure:
   a) De-oxidation of the sample in a 1 M HCl solution (30 to 60 mn) and rinsing with ultra pure water (5-10 MΩ.cm)
   b) immersion of the sample in the chosen bath for timed durations
   c) sample removal and ultra pure water rinsing
   d) drying with dry compressed air
   e) weighing (precision: 0.1 mg)
   f) microscope observation
   g) back to step a)

If not specified T= 30° C. At the end of a test, sulfur is extracted by chloroform ($CHCl_3$), which was chosen because of its very high extraction yield, its low boiling point (61.2 °C) and its low toxicity compared to other chlorinated solvents.

Aluminum in sulfuric acid

As can be observed on Figure 2, corrosion of Al reaches a maximum at intermediate H_2SO_4 concentration while it is decreasing at low and very high concentrations.

Sulfur synthesis typically happens at very high sulfuric concentration. Note that the usual EP mixture is also highly concentrated in H_2SO_4 (~ 16 mol/L).

The characteristic odor of H_2S was also detected and we evidenced its synthesis by bubbling the exhausted gas in a zinc acetate solution (1 mol/L). We noticed a white precipitate of zinc sulfide ZnS.

$(CH_3CO_2)Zn + H_2S = ZnS + 2 CH_3CO_2H$ (6)
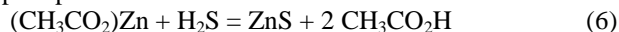
At lower concentration ($[H_2SO_4]<16$ mol/L), predominant reaction seems to be hydrogen synthesis:

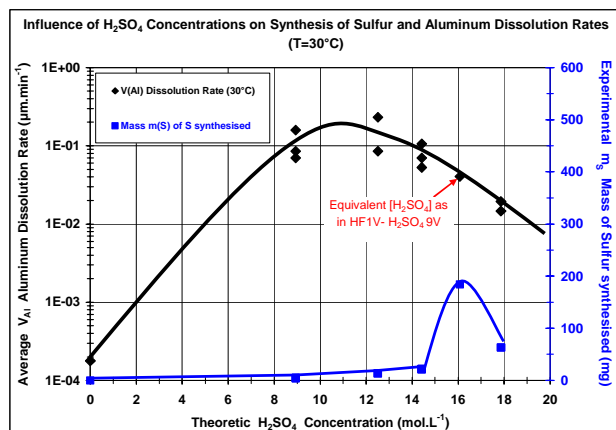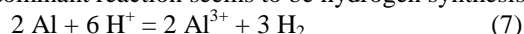$2 Al + 6 H^+ = 2 Al^{3+} + 3 H_2$ (7)

Figure 2: Corrosion of aluminum and production of sulfur in function of sulfuric acid fraction.

Aluminum in hydrofluoric acid

Aluminum corrosion in hydrofluoric acid solutions was tested at 2.29 mol/L and 22.87 mol/L.

- Al removal rate is very high in concentrated hydrofluoric acid solutions. HF is much more aggressive towards Al than H_2SO_4. The etching rate is ~ 4 µm/min at 2.29 mol/L and ~ 8 µm/min at 22.87 mol/L.
- A grey precipitate is formed (probably AlF_3). This precipitate slightly sticks on Al and is easily removed with water.

Al in 1 vol. HF – 9 vol. H_2SO_4 EP baths:

This mixture is characteristic of baths used at KEK and DESY. The associated concentration is 2.29 mol/L of HF and 16.08 mol/L of H_2SO_4.

Two experiments have been carried out in order to detect a possible impact of alumina layer: for one experiment, oxide was first removed by soaking the aluminum sheet in HCl 1 mol/L during 30 min, while the second one was undertaken without prior HCl treatment (See figure 3).

These experiments were run for ~50 hours. The following observations have been made:
- Corrosion of aluminum is several orders of magnitude lower than inside separated acids
- At the end of the experiment, no sulfur is found in the mixture.
- A few amount of bubbling is noticed.
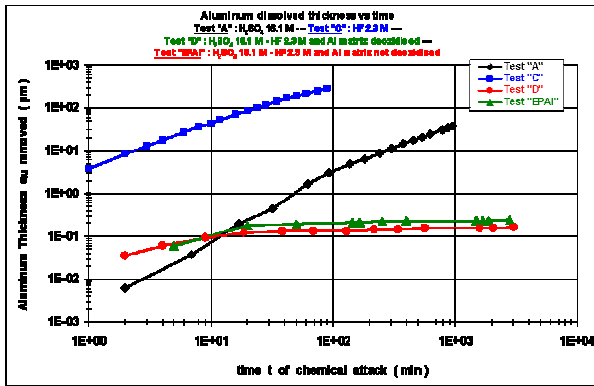- No precipitate is detected in the bath at the end of the experiments.

Figure 3: Comparison of Al dissolution rate in HF (blue), H_2SO_4 (black), and EP mixture (green). In red: EP mixture without prior etching (see text for exp. details)

Al in other bath compositions:

Various bath's compositions have been tested. It can be observed that sulfur generation depends a lot from the HF content (see some examples in Table 1).

Table 1: Sulfur generation in function of bath composition

Test #	Volumic composition			Sulfur synthesis	
	HF	H_2SO_4	H_2O add	Time (minutes)	Sulfur mass (mg)
A	0	9	1	955	184.2
E*	0.1	9	0.9	5930	9.9
J	9	1	0	228	0

*H_2S detected after17 min.

The more HF, the less sulfur is produced, probably by "diluting" H_2SO_4 as the constitutive water content of HF is higher. This indication might be very useful for further modifications of bath composition. Indeed, increasing HF content is also a way for improving lifetime of EP mixture [12].
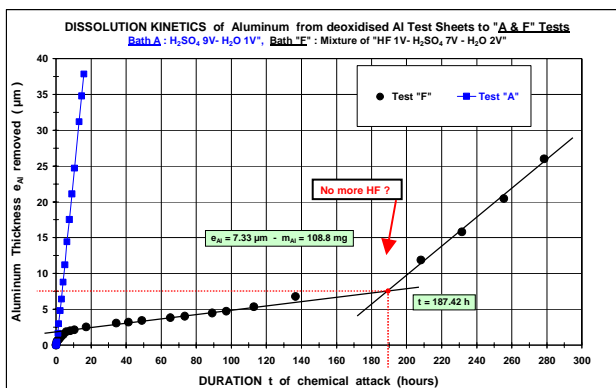

Figure 4: Al dissolution kinetics within the classic EP solution (blue) and with a lower H_2SO_4 content. Corrosion of aluminium is far more less as long as there is enough HF inside the solution.

Moreover, when HF content decreases (which normally happens during the EP process as HF is evaporating as well as consumed by the Nb dissolution process), active corrosion of Al recovers, as can be noticed e.g. on figure 4.

CORROSION IN WITH APPLIED VOLTAGE

Actual EP was studied in a special device with a rotating anode described elsewhere [13]. When voltage is applied in an EP set-up, strong H_2S smell can be detected, and yellow-brown deposits are observed on samples and vessel walls. Slow but continuous corrosion (dissolution) of Aluminum cathode is observed.

Table 2: Mass of sulfur M_S generated during actual EP

Test#	M_S calculated* (mg)	Measured M_S (mg)
Rot A	1,07	21,1
Rot B	3,27	113,8

*compared to Al dissolution as in reaction (4)

The sulfur production is strongly enhanced compared to the situation without voltage, as can be noticed in table 2, probably due to the cathodic polarization of the cathode.

Aging

As was already observed in the case without voltage, after long term experiment, when HF has probably much decreased, heavy corrosion of the Al cathode recovers (see figure 5).

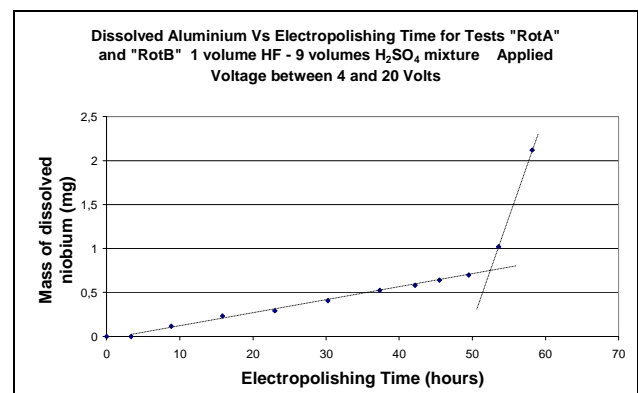Note that EP conducted inside a 3 vol HF-6.72 vol H_2SO_4 -0.28 vol H_2O did not produce any S.

Figure 5: Al dissolution during a classic EP of Nb samples. After a long term experiment, when nearly all HF has been consumed, enhanced Al corrosion starts.

CONCLUSION

The relative composition of EP mixture in HF and H_2SO_4 has proven to be a critical issue for the protection of aluminum cathode as well as for the synthesis of solid sulfur. Solid sulfur is systematically observed with the

classical 1-9 EP composition, and it is hardly rinsed as it is not water soluble. Its presence could explain that field emission is often observed in EP cavities.

Enhancing the HF proportion seems to reduce the sulfur generation, and is thus more favorable. Some additional studies to improve rinsing efficiency (e.g. with chlorinated solvents) are also needed.

Corrosion of Aluminum in highly concentrated H_2SO_4 solution cannot be prevented, but it keeps low as long as there is enough HF inside the solution, due to the formation of little soluble AlF_3. Meanwhile, enhancing HF content ("diluting" the H_2SO_4 fraction) might enhance slightly Al corrosion, but seems to prevent solid S formation.

Nevertheless, due to its very low redox potential, Al is not likely to form any metallic particles and will keep in solution mainly in the form of Al^{3+} salts, which are most of the time water soluble. Appropriate rinsing should overcome this problem quite easily.

Attempts to find another cathode material have already been done. Copper, Niobium as well as Platinum leave metallic particles on the Nb surface and have been discarded. Further experiments can be foreseen.

In all the case, aging of the EP bath has to be carefully monitored, so that one is sure to have still enough HF inside solution.

REFERENCES

[1] M. Stern and C.R. Bishop, "8 : Corrosion and electrochemical behavior", in Colombium and Tantalum, F.T. Sisco and E. Epremian, Editors. 1963, John Wiley and Sons: New York. p. 304-346.

[2] H. Diepers, et al., "A new method of electropolishing niobium". Physics Letters, 1971. **37A**(2): p. 139-140.

[3] K. Saito, et al. "R & D of superconducting cavities at KEK". in 4th workshop on RF Superconductivity. 1989.

[4] L. Lilje, et al., "Improved surface treatment of the superconducting TESLA cavities." Nuclear Instruments and Methods in Physics Research Section A : Accelerators, Spectrometers, Detectors and Associated Equipment, 2003: p. in press.

[5] Steinhau-Kuehl N. et al, this conference

[6] C. Vargel, ed. "Corrosion de l'Aluminium". Technique et Ingénérie Série Matériaux. 1999, Dunod: Paris.

[7] A. Despic and V.P. Parkhutik, "Electrochemistry of Aluminum in aquous solution and physics of its anodic oxide". Modern aspect of electrochemistry, 1989. **20**: p. 401-504.

[8] P.A. Malachesky, "Aluminum", in Encyclopedia of electrochemistry of the elements, A.J. Bard, Editor. 1976: New York. p. 63-165.

[9] J. Diggled, T.C. Downie, and W.C. Goulding, "Anodic oxide films on Aluminum". Chem. Rev., 1969. **069**: p. 365-405.

[10] H.P. Godard, "Aluminum", in The corrosion of light metals. 1967, John Wiley & Sons: New York. p. 3-218.

[11] C.D. Mac Quarry and P.A. Rock, "Chimie Générale". 3rd. ed, ed. D. Boeck-Wesmael. 1992, Bruxelles.

[12] F. Eozenou, C. Antoine, A. Aspart, S. Berry, B. Malki, "Efficiency of electropolishing vs bath composition and aging", this conference.

[13] See e.g. TESLA Collaboration Meeting at DESY Zeuthen, 21st-23th January 2004 http://www-zeuthen.desy.de/tesla2004/programm.html