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CORROSION OF ACCELERATOR VACUUM SYSTEMS: RISKS AND PREVENTION

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ABSTRACT

Although not exposed to a strongly aggressive environment, the very sensitive equipment constituting the vacuum systems of accelerators and storage rings requires some special attention with respect to corrosion prevention. The aim of this communication is to recall some characteristics of the materials commonly used in UHV systems and to draw the attention of vacuum specialists to various cases of corrosion encountered in accelerators. They can be classified into 3 main groups: (1) Atmospheric corrosion due to the contact of the vacuum components with aggressive gas species such as ozone, nitrogen oxides and halogens in the presence of humidity, (2) Corrosion in cooling systems which are nowadays often part of the vacuum vessel and (3) dry corrosion due to a reaction between a metal and a molten metal. Past experience in the operation of accelerators and storage rings has shown that weak points with respect to corrosion can be divided in two classes : (i) intrinsic weak points which must be tolerated such as the thin walls of metallic bellows or the bimetallic contacts in brazed insulating feedthroughs and (ii) Extrinsic weak points which have been introduced by inadequate design, choice of material or heat treatment, etc. These weak points can be minimized by a careful examination of the available technical alternatives and by an appropriate choice of both material and heat treatment.

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1. INTRODUCTION

The delicate equipment generally constituting accelerator vacuum systems can suffer from corrosion, although its environment is not strongly aggressive. Furthermore, the importance of a minor aggression cannot be judged, as is usual, by assessing the weight of material lost because the leak tightness in some critical parts of the system may rely on the integrity of a fraction of a cubic millimeter. A vacuum failure necessitates a costly interruption in the operation of an accelerator which can spread over several days if rebaking is mandatory. It is hence very important to consider the risk of corrosion as non negligible and in order to prevent failures, to integrate at a very early stage in the design of an accelerator vacuum system the prevention of the corrosion risks.

In this paper we will review for an audience of vacuum specialists the most common aggressive media in an accelerator and draw the attention to the various types of weak spots typical for vacuum systems, taking into account past experience in this field. Starting from these basis, some simple preventive rules concerning the design and the fabrication of vacuum systems will be given.

2. ENVIRONMENT AND AGGRESSIVE AGENTS

The most widely encountered type of corrosion in accelerator vacuum systems is atmospheric corrosion, due to the contact of the metallic components with the atmosphere. Atmospheric corrosion is an electrochemical process^{1, 2)} taking place in a thin film of electrolyte solution on the metal surface. In an accelerator, this process is enhanced by the radiation³⁾ emitted by the circulating beam(s). The humidity content of the air is thus a critical parameter in determining the corrosion speed. In systems not exposed to radiation, it is usually admitted that below 60% relative humidity (R.H.)⁴⁾, the corrosion rate is negligible. This threshold is greatly affected by irradiation and can be lowered to 15-30% R.H., depending on the irradiation intensity⁵⁾. The origin of this effect is not linked directly to an activation of the oxidation rate but to the creation of ozone, nitrogen oxides⁶⁾ and metastable oxidized species which are especially reactive. The presence of these metastable oxides (especially nitrogen oxides) is largely responsible of the enhancement of the corrosion rate in the close vicinity of a radiation source. On contact with the moisture film present on the surface, these reactive species form nitrogen based acids which lead to the corrosion of sensitive materials. Furthermore, these radiolysis products are also active cathodic depolarizers⁵⁾ and again enhance the corrosion speed.

Another possible source of strongly aggressive agents is the decomposition under irradiation of halogenated organic compounds like polyvinyl chloride (PVC) or chloro-fluoro-carbons (CFC), thus liberating free halogens^{7, 3)} especially chlorine, one of the worst pitting inducers^{8,9)}. It should be also noted that nitrate ions inhibit the ions of stainless steel¹⁰⁾ and of aluminium¹¹⁾ by chloride ions. Nevertheless, it would not be wise to consider this property as a sufficient protection against pitting.

Another source of nitrogen oxides in accelerators comes from the spurious electrical discharges which can appear in the presence of a high electrical field, especially in a confined area.

When corrosion has been initiated, it can continue with reduced R.H. as the corrosion products¹²⁾ may act hygroscopically to form a solution in equilibrium with a lower R.H.. The corrosion products may increase the conductivity of the electrolyte solution and hence the corrosion rate. Furthermore, depending on the type of conductivity of these products, galvanically enhanced corrosion can also take place¹³⁾.

Other cases of corrosion may be encountered in water-cooled vacuum systems due to the erosion/corrosion of the cooling pipes which are, especially in electron machines, often part of the vacuum vessel. The corrosion rate depends greatly on the speed and purity of the demineralized water. Impurities like chlorine can have a drastic effect at a very low concentration level. Galvanic couples or water circuits built of dissimilar materials (e.g. aluminium/copper) can increase greatly the corrosion rate and/or lead to the blockage of the cooling-pipes.

Lastly, cases of dry corrosion have been observed when a brittle solid solution is formed between two metals, e.g. during the vacuum brazing of two materials. This effect is strongly enhanced by the presence of high stresses and can lead to a failure of the component if it is reheated to the fusion temperature of the solid solution after its formation.

3. WEAK POINTS

The design of an accelerator vacuum system is determined by many parameters such as degassing rates, bakeability, thermal conductivity, electrical insulation etc... which force the designer to introduce components, intrinsically weak with respect to corrosion. On the other hand, components can be weakened by an improper design or fabrication methods. In the following paragraph, based on the past experience in accelerator operation, some possible weak points will be classified according to the above distinction into two classes: intrinsic and extrinsic weak points.

3.1 Intrinsic weak points

To the first category belong all thin-walled elements (less than 1 mm) such as bellows, windows and some types of feedthroughs. Apart from their obvious fragility these elements, which in many cases (e.g. bellows) allow relatively large mechanical deformation, are often heavily stressed. Electrical feedthroughs are generally submitted to potentially dangerous thermal treatments (brazing).

The second category is defined by the resistance of the base material to the aggression of the accelerator atmosphere. With the exception of the noble metals, the immunity of most usual materials relies on the passivity of a

surface oxide layer. A chance breakdown of the passive film can initiate the development of corrosion. The resistance of austenitic stainless steel is good in the normal accelerator atmosphere (and more specifically against nitric acid aggression), but the immunity of aluminium is more problematic as the passivation layer is not so stable. In fact, alumina is soluble at a PH value lower than 3 and dilute nitric acid is known to be aggressive with respect to aluminium. In accelerators therefore, the reliability of thick aluminium parts is generally acceptable but thin aluminium components deserve special attention. Copper is subject to a strong corrosion through oxidizing acids (e.g. nitric acid). Alloys with thermal expansion comparable to that of ceramic (e.g. Kovar, Dilver ...) are usually prone to heavy corrosion when placed under unfavourable conditions. In accelerators many failures of high voltage feedthroughs (e.g. ion pump feedthroughs) based on these materials have been reported.

The fabrication of vacuum components frequently involves a junction through the welding or the brazing of two parts. Even when done under good conditions, these operations quite often lead to a modification of the metallurgical structure due to the high temperature during the process. Such modifications can have a drastic influence on the corrosion resistance of materials although, generally, failures of this type are due to improper processes or design and will be treated in the forthcoming paragraph.

Because corrosion is an electrochemical process, the corrosion rate is greatly enhanced by the presence of electrochemical potential difference in the electrolyte layer. One of the major sources for such differences are bimetallic contacts, where the less noble metal will be corroded¹⁴⁾. The gravity of the danger is related to the standard potential difference¹⁵⁾ between the two materials and, due to the normally low conductivity of the electrolyte film, it is generally confined to a region close (~25 mm) to the contact. The ratio of the exposed areas is also an important¹⁶⁾ parameter. Especially harmful is the case of a small cathodic (e.g. aluminium) region surrounded by a large anodic region (e.g. copper). Typical weak points of this nature are brazed junctions. Often brazing materials are based on relatively noble metals: Cu, Ag, Au and lead to an enhanced attack of the adjacent material.

Other points of potential danger, which are often difficult to eliminate by design, are heavily stressed zone, which may lead to the rupture of the passivation layer and further to stress corrosion¹⁷⁾ (or corrosion fatigue under dynamic conditions). Some materials are more prone to this type of corrosion. For aluminium alloys¹⁸⁾, the 6000 series is relatively immune, but series 5000 can be affected and series 7000 is the most sensitive. Lastly, as stated in Chapter 2, zones subjected to a high radiation flux are of potential danger because of the higher concentration of metastable corrosive species.

3.2 Extrinsic weak points

These are introduced by an improper design or fabrication of a vacuum component. As opposed to the former type, they can, and should, be eliminated.

A first set in this category concerns all inappropriate metallurgical structures prone to corrosion. These structures can result, for example, from:

- a wrong choice of material;
- a bad combination of material and heat treatment;
- an improper welding technique.

In vacuum technology, a special heat treatment is often used to reduce the degassing rate of stainless steel. This treatment consists of heating to high temperature (900°C) under vacuum¹⁹). If such a treatment is applied to a stainless steel of normal carbon content, a precipitation of carbide (sensitization) will, among many other consequences, considerably reduce the corrosion resistance of the steel²⁰). The same phenomena might occur during high temperature brazing of vacuum components (feedthroughs). A perturbed and especially sensitive zone is formed around welds²¹), especially when a severe porosity may locally reduce the wall thickness ensuring leak tightness to a fraction of a millimeter.

The danger of galvanic contact has been stressed in the previous paragraph. Any unnecessary contacts must be avoided. As an example, the use of a copper gasket on an aluminium flange would fall in this category and could be very harmful.

Another particularity of vacuum technology is the careful cleaning needed by the components. Although the cleaning must be sufficient, it should not be too strong and lead on some materials like aluminium alloys to etching which could destroy the surface finish of sealing surfaces. Lastly, the pieces must always be thoroughly rinsed, since cleaning product residues are generally aggressive. In this respect bellows require special attention when it is difficult to rinse completely between undulations.

A combination of the important agents leading to corrosion (water vapour and radiolysis products from air) create particularly unfavourable conditions. Confined volumes close to a radiation source or cold spots on or in the vicinity of the vacuum system are weak points which can often be eliminated. Similarly, the exposure to radiation of halogen containing materials (PVC, CFC...) in contact or close to the vacuum chamber constitutes a real danger, even for the most corrosion-resistant stainless steel.

4. CORROSION PREVENTION

Corrosion prevention is not a primary aspect in the design of an accelerator vacuum system and the designers are often confronted with other technical problems which can divert their attention from potential corrosion risks. As the environment in accelerators cannot be considered as strongly aggressive, a good rule for corrosion prevention at the stage of design is to avoid, if possible, the superposition of several weakening factors at the same place (i.e. a high voltage feedthrough made with corrosion sensitive material in a badly ventilated zone, or a weakened material as part of a bimetallic contact).

In the choice of materials, those presenting a good resistance to nitric acid should be preferred when possible. A simple comparative test consists of immersing the materials in a dilute solution of nitric acid (e.g. 10% volume). It must be stressed that this test is only comparative and does not give any indication concerning lifetime. Tests in a climatic cabinet in which the humidity and the nitrogen oxide content can be adjusted can lead to a better estimate of the real lifetime.

A careful control of the atmospheric humidity is the most important rule to ensure a good protection. This can be achieved by a proper air conditioning system (ideally less than 50% R.H.). A delicate piece of equipment is also effectively protected by raising its temperature above the mean temperature, thus reducing locally the R.H.. A rule of thumb is that a temperature increase of 10°C above the mean temperature is usually sufficient to reduce the R.H. below 60%.

Adequate shielding should be provided to limit the irradiation of the air. The creation of confined pockets of humid air should be avoided. Halogen containing materials exposed to radiation and in contact with parts of the vacuum system must be strictly prohibited. A good rule is to forbid, during the storage and the manipulation of any equipment, the use of halogen containing packing material. Alternatives can be found to replace these material when they are unavoidable (e.g. water or alcool to replace CFC as cooling medium).

During the fabrication of vacuum components the quality of welds should be carefully checked to avoid a lack of penetration or a porosity reducing the wall thickness. Thermal treatments must be adapted to the type of material used, especially for stainless steel where the low carbon grade must be used whenever a high temperature treatment is foreseen. All traces of brazing flux, generally rich in halogens, (especially chlorine,) must be carefully eliminated as also for cutting oils containing chlorinated additives, which are unstable under irradiation.

Special attention must be paid to thin-walled equipment. Whenever possible, corrosion-resistant equipment (stainless steel) must be used. In the case of aluminium, a good protective coating (e.g. sealed anodic layer) is mandatory. In this case, the layer must be carefully preserved during all manipulations in order to avoid scratches. Further protection by a dry inert gas (e.g. nitrogen) to prevent the contact of the equipment with aggressive species has also been proposed²²).

For electrical feedthroughs, a possible solution is a combination of low carbon stainless steel (e.g. AISI 304L) for the metallic parts and gold-nickel as brazing material.

5. CONCLUSION

Corrosion of the vacuum system may lead to failures which will stop the accelerator and require the replacement of the defective equipment. Such failures can be avoided by the identification of the potential weak points with respect to corrosion. Some of these can be eliminated at the design stage; others can be avoided by proper care during the fabrication of the equipment; some must be accepted, but the designer should always try to eliminate the juxtaposition of several corrosion prone features at the same place. Lastly, the control of the atmospheric humidity, especially around sensitive equipment, remains the most efficient way of mastering corrosion problems in accelerators.

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