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In situ electrochemical AFM, *ex situ* IR reflection–absorption and confocal Raman studies of corrosion processes of AA 2024-T3

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ABSTRACT

The corrosion processes of AA 2024 were analysed via the combined approach of advanced *in situ* and *ex situ* analytical tools. Firstly, IR reflection–absorption spectroscopy enabled the identification of a pseudo-boehmite layer on initial surface, which remained present also after the *ex situ* spectroelectrochemical treatment at different potentials. Secondly, formation of oxyhydroxides was confirmed by confocal Raman spectroscopy. To get a deeper insight into the morphology changes, a three-electrode *in situ* electrochemical AFM cell was constructed. The results of *in situ* measurements revealed a gradual increase in the surface roughness. Trenching around intermetallic particles and corrosion deposits were also observed.

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1. Introduction

Numerous papers have been reported on corrosion processes of AA 2024 [1–13] and one may wonder whether there is anything important to add. The processes have already been divided into different stages characterised by the localised attack around isolated intermetallic particles like dissolution and trenching, developing of domes and rings of corrosion products, clustering of corrosion products, grain boundary attack and pit formation. The initiation of the localised corrosion is often ascribed to the presence of different intermetallic particles and their galvanic coupling with the surrounding matrix [4,14], while stable pit formation have been associated with the clustering of the corrosion products [2,3]. The trenching around the intermetallic particles is also a matter of debate, the classical cathodic mechanism being ascribed to the strong pH gradient near the particle and the higher solubility of the oxide at elevated pH [15], but the alternative anodic mechanism refers to a Cu depletion around the intermetallic particles

and the subsequent lowering of the pitting potential of this region [16]. Different studies identified a variety of the compositions of the intermetallic particles (S-Al₂CuMg (about 60%), θ-Al₂Cu, Al–Cu–Fe–Mn and (Al,Cu)_x(FeMn)_ySi with a manifold range of compositions), which crucially depended on the additives and preparation procedures of AA 2024 [2–4,14,16–22]. In addition, for aluminium alloys the processing conditions during rolling and mechanical grinding, i.e. exposure to extensive shear, were reported to lead to the segregation of the alloying elements to the surface [1,5] differences in surface roughness and porosity [1], and consequently the formation of a corrosion more susceptible near surface deformed layer (NSDL) [1,6,23,24]. Furthermore, the application of a constant load to a thin sheet sample of AA 2024 resulted in an intergranular stress corrosion cracking [7], which also appeared in extruded AlMgSi(Cu) model alloys with increasing amount of Cu and depended on the thermomechanical treatment [25].

It has often been suggested that using a combination of various techniques would be the best approach to gather more information on the corrosion processes of aluminium alloys. A transmission electron microscopy (TEM) [17] or scanning electron microscopy (SEM) has often been combined with energy-dispersive X-ray spectroscopy (EDX) [14,16,18] and X-ray photoelectron spectroscopy

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(XPS) [19]. Although numerous studies have been made with the standard electrochemical [14,16,20] and microscopic techniques [2–4,14,16,21,22] investigations of different aluminium surfaces using the *in situ* electrochemical atomic force microscopy (AFM) approach (Al-6061-T6 [26], AA 2024-T3 [15], Al₈₈Ni₈Ce₄ amorphous ribbons [19]) are not so common. There still remain open challenges to confirm firm conclusions about the early or late stages of the corrosion processes, the influence of intermetallic particles on the formation of the trenches around them, pitting corrosion or dissolution of matrix already obtained by other techniques [2–4,14,16–22]. For aluminium alloys it has been reported that the inherent corrosion resistance is due to the formation of a protective aluminium oxide [18,27] that was developed on the surface of the alloy in air or solutions. Vibrational techniques, Raman and infrared (IR) can offer important conclusions about the formation of oxides, oxyhydroxides and hydroxides under different exposures to electrolytes.

In this article the main idea was to follow extensively the changes on the surface of AA 2024 during exposure to sodium chloride environment using techniques that probe the sample on different size scales: (i) IR technique that gives averaged information about the surface dominated by the matrix; (ii) micro-Raman, which enables a spatial resolution of at least 1 μm and, (iii) AFM that can provide results on the micro- and nanoscale levels. Consequently, a question arises, whether it is possible to tie together the results obtained by these three techniques, each of them not only being performed on a different size scale but also giving a slightly different type of chemical/electrochemical information.

A short background on the application of these techniques in the investigation of AA 2024 will be given first.

(i) A valuable and extensive bases on IR emission and IR absorbance characteristic of alumina phases (boehmite, diaspore, gibbsite and bayerite) was given by Frost et al [8–10], and Ruan et al [28], who in addition studied dehydroxylation of goethite (α-FeOOH) [29,30], also from the point of view of the effect of aluminium substitution [31]. However, the detection of the evolution of passive layers on reflective substrates (AA 2024 as well) demands infrared reflection–absorption (IR RA) technique, where the measurements are performed with P-polarised light and under near grazing incidence angle (NGIA) conditions, for example at 80° [32]. The resulting longitudinal optical (LO) modes are usually shifted to higher frequencies with regard to transversal optical (TO) modes obtained in the IR absorption measurements, therefore the assignment of LO modes is not straightforward. Few reports exist about the detection of aluminium oxide layers on alloys (AA 2024 [11,12], AA 1050 [33], Al [34]), but when the AA 2024 surface is exposed to hydration a pseudo-boehmite phase is developed [11–13]. In addition, *ex situ* IR RA approach, enables to follow the evolution of the oxyhydroxide–oxide phases with exposure of the alloy to certain potentials before and after corrosion potential, but such studies are rare [11]. Even though the IR RA spectra give information about the vibrational bands of quite thin (from few tenths of nm) oxide layers formed on metallic substrates, an open question remains whether this technique is sensitive enough to enable the detection of oxides of various intermetallic phases since their surface density is small and distribution rarely uniform over the Al surface. According to our knowledge no records exist about the detection of copper oxide bands of intermetallics with the IR RA technique. A characteristic IR RA triplet with LO modes at 620, 555 and 515 cm⁻¹ was reported to occur in case of CuO coatings on Al substrate with an LO–TO splitting of 20–45 cm⁻¹ with regard to IR absorbance measurements [35,36]. *Ex situ* IR RA measurements have mainly been performed on various sol-gel coatings deposited on AA 2024 [11,13,37,38], primarily to provide information about the bonds that are most likely to break and subsequently, to undertake actions to the modification of the coating composition.

(ii) Among the Raman studies most of the work was devoted to various coatings deposited on AA 2024 [39–44]. Moreover, the micro-Raman spectroscopy has already been used in our group to study degradation of the sol-gel protective coatings on AA 2024 during forced anodic degradation; either *ex situ* [37], or *in situ* in a three-electrode custom-made Raman spectroelectrochemical cell [38]. In the field of hydroxide–oxyhydroxide alumina phases Raman spectra were reported by Frost et al [9], and H.D. Ruan [31] on either synthesized powders or naturally occurring minerals. The largest challenge with regard to the unprotected alloy, however, remains the Raman spectroscopic examination on an aluminium alloy directly. There have already been made studies of AA 2024 [45], AA 6061 [46], Al-32% Co [39], and the results indicated the presence of aluminium oxide, as well as various hydroxides and oxyhydroxides, but the exposures were made at different times and electrolyte conditions. Since Cu is the most important alloying element of AA 2024 the question arises if its oxidation can also be evident as corrosion processes proceed. For instance, the work on multiphase CuAlBe alloy exposed to NaCl electrolyte [47] confirmed the presence of CuO, Cu₂O, CuCl₂ and Al₂O₃, but the bands of the latter compound were of very low intensity [47]. Alternatively, *in situ* surface enhanced Raman spectroscopic (SERS) technique can be applied for the detection of oxides–oxyhydroxides, as for example in the case of iron, nickel, chromium and stainless steel, which confirmed the formation of passive films of hydroxide/oxide species [48] or the characterisation of different Cu-oxide aggregates that were formed within the porous alumina [49].

(iii) The atomic force microscopy (AFM) and scanning tunnelling microscope (STM) has been known as powerful tools for the characterization of the coatings and other materials. STM is limited to conductive samples [50], while AFM enables analyses of conductive or non-conductive layers [51] on a nanoscale level. Both techniques (STM [52–55] and AFM [56]) offer the possibility of the investigation of materials in the liquid environment, however, the AFM studies, which started already in the nineties [18,26,57–61], have larger potential to follow the evolution of the corrosion processes on various alloys/metals due to formation of oxyhydroxide–oxide layers. It was found that AFM enabled the study of the shape evolution during corrosion processes at a high lateral resolution, for example the deposition of precipitates, formation of trenches in near proximity of intermetallic inclusions, as well as highly localized processes at the cellular boundaries or grain boundaries [17,26,62]. During all these years in the field of corrosion, the term *in situ* has been used for two different types of measurements: (i) analyses performed only in electrolytes or solvents, *i.e.* a drop on the investigated surface or an application of a commercial fluid cell (thin Al film [57], AA 2024-T3 [18,58], high strength steel [63], CuAlBe alloy [47]) or (ii) an application of the potential on a working electrode in an *in situ* AFM electrochemical cell (Al-6061-T6 and stainless steel SS-304 [26] and 304 L [64], AA 2024-T3 [15], iron [59], stainless steel 304 [65] or 304 L [64,66], austenite stainless steel [67], copper [60,61,68,69] Al₈₈Ni₈Ce₄ amorphous ribbons [19]). While the former studies have been reasonably frequent, the studies with applied potential have been much rarer. The literature search revealed that most of the *in situ* AFM corrosion studies of the metals/alloys either immersed [18,57,58] or treated under potentials [15,26,60,65,68,69] were obtained in the commercial fluid AFM cells characterized with a very low volume (in most cases 0.1 ml), which can consequently induce large changes in the local pH values and influence the reliability of the results [18]. Consequently, in order to increase the volume of the electrolyte, custom-made *in situ* electrochemical AFM cells made of Teflon or polycarbonate were designed and mounted under the scanner of the instrument [19,61,64,67]. Anyhow, the consequence of the instrumental complexity of the *in situ* electrochemical AFM approach was also the *ex situ* performance of the surface AFM

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