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# Flow microcapillary plasma mass spectrometry-based investigation of new Al–Cr–Fe complex metallic alloy passivation

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## ABSTRACT

Al–Cr–Fe complex metallic alloys are new intermetallic phases with low surface energy, low friction, and high corrosion resistance down to very low pH values (0–2). Flow microcapillary plasma mass spectrometry under potentiostatic control was used to characterize the dynamic aspect of passivation of an Al–Cr–Fe gamma phase in acidic electrolytes, allowing a better insight on the parameters inducing chemical stability at the oxyhydroxide–solution interface. In sulfuric acid pH 0, low element dissolution rates (in the  $\mu\text{g cm}^{-2}$  range after 60 min) evidenced the passive state of the Al–Cr–Fe gamma phase with a preferential over-stoichiometric dissolution of Al and Fe cations. Longer air-aging was found to be beneficial for stabilizing the passive film. In chloride-containing electrolytes, ten times higher Al dissolution rates were detected at open-circuit potential (OCP), indicating that the spontaneously formed passive film becomes unstable. However, electrochemical polarization at low passive potentials induces electrical field generated oxide film modification, increasing chemical stability at the oxyhydroxide–solution interface. In the high potential passive region, localized attack is initiated with subsequent active metal dissolution.

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## 1. Introduction

Complex metallic alloys (CMAs) are a new class of crystalline intermetallic phases characterized by a complex crystallographic structure. They are organized in large unit cells, containing hundreds of atoms arranged in highly symmetric clusters, and often considered as stable approximants of quasicrystals [1,2]. Within the CMAs family, Al-based CMAs are promising for future industrial application [2,3]. They are developed to be used as functionalized coatings [4–6] to enhance the aluminum corrosion resistance. Al-based CMAs exhibit a unique combination of surface properties [2,3,7,8], such as low surface energy, low friction coefficient and high stability in a broad pH range [9,10], which depend on their chemical composition rather than on their structural complexity [9,11,12]. Consequently, many of these properties are tightly related to the oxyhydroxide layer, which spontaneously forms on the surface [13]. This nm-thick oxyhydroxide layer, also known as passive layer, continuously undergoes dynamic processes associated with film growth at the metal–oxyhydroxide interface and chemical dissolution at the oxyhydroxide–solution interface.

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A comprehensive understanding of these processes is therefore necessary to guarantee the material's properties in *operando* conditions for longer service times.

Surface analytical techniques provide useful information about the surface chemical composition, structure, topography and mechanical and electronic properties of passive films [14]. However, they are mainly *ex situ* methods and consequently no mechanistic information about film dynamics can be retrieved. They are usually used in combination with electrochemical methods to determine kinetic data [14]. However, none of these techniques allow full characterization of the dynamic of passivation (including chemical dissolution) at the oxyhydroxide–solution interface.

The electrochemical quartz crystal microbalance (EQCM) proved to be suitable to monitor changes in the passive film induced by electrochemical film growth and chemical dissolution processes at the oxyhydroxide–solution interface with a sub-monolayer mass change sensitivity [15–17]. It could be determined that an increase in the polarization potential leads to an increase of the passive film thickness associated with a significant cation dissolution from the passive film surface. The obtained information remains nevertheless averaged mass changes. Therefore, this method, despite its extremely high sensitivity, only suits for model homogeneous materials.

Over the past years analytical chemistry methods have gained increasing interest in corrosion science. They can provide quantitative information about the element-specific releases even at early corrosion stages, allowing better characterization of the passivation

dynamics at the oxyhydroxide–solution interface, especially when electrochemical methods are at their current detection limits. In particular, plasma spectroscopy methods, i.e. inductively coupled plasma optical emission spectrometry (ICPOES) and inductively coupled plasma mass spectrometry (ICPMS), present interesting characteristics, such as “fast” multi-element detection, high sensitivity and trace amount detection limits. Nonetheless, these methods are currently mainly used offline, by means of immersion tests, in which the dissolution of a sample in an aqueous environment is followed over time by sampling aliquots of the solution. Analyses are performed afterwards by ICPOES or ICPMS. The whole procedure is consequently time- and sample consuming as well as affected by sampling induced uncertainties.

Hyphenated methods, based on online coupling of an electrochemical flow cell and different downstream analytical techniques [18–26], offer several advantages over conventional immersion tests. Atomic Emission Spectroelectrochemistry (AESEC) [18,19,27–31] or coupling of a microelectrochemical flow cell to an ICPMS [20,21,26] allow determining instantaneous element-specific dissolution rates. Flow microcapillary plasma mass spectrometry on the other hand provides local, time-resolved and element-specific information of corrosion processes under low laminar flow, close to natural convection. It was already successfully applied for corrosion investigations of passive and active systems at open-circuit potential (OCP) [23,32–34]. Coupling of this element-specific technique to electrochemical measurements can be particularly interesting, especially for passive metals, because it provides combined information about transient electrochemical processes at the metal–oxyhydroxide interface and chemical element-specific dissolution at the oxyhydroxide–solution interface.

An important aim of the current study is therefore to present the specifically developed electrochemical microcell for flow microcapillary-based analysis under potentiostatic polarization and to demonstrate its applicability to investigate the dynamic passivation processes of a polycrystalline Al–Cr–Fe gamma phase in acidic electrolytes. This phase exhibits good passivation in extreme pH ranges [9] and is ready to be implemented as a coating in industrial application. Ura et al. [9] showed that the stability of the Al oxyhydroxide layer formed on the Al–Cr–Fe gamma phase relies on the Cr enrichment at the outermost layer. Another relevant aspect for these Al-based alloys is the composition and thickness changes that will be induced in the passive film at long air-aging times [35].

The effect of anodic potentiostatic polarization and air-aging on element-specific dissolution rate were consequently investigated in sulfuric acid at pH 0 by flow microcapillary plasma mass spectrometry analysis under potentiostatic polarization. The strength of this novel experimental method is the simultaneous characterization of both interface reactivity and the identification of discrepancies in the experimental results, which can arise from materials heterogeneities or be inherent to each of the methods used. Most of the published studies only consider one characterization method and, therefore, miss some of the interface processes occurring during passive film formation. The passivation dynamic in a more aggressive environment, i.e. in presence of chlorides, resulting in local destabilization of the oxyhydroxide layer at the oxyhydroxide–solution interface, is also well characterized.

## 2. Materials and methods

### 2.1. Samples and solutions

The investigated polycrystalline powder-sintered gamma phases,  $\text{Al}_{64.2}\text{Cr}_{27.2}\text{Fe}_{8.1}$  (at. %), were prepared at the “Laboratoire de Science et Génie des Matériaux et de Métallurgie” (Nancy, France) [36]. The

polycrystalline gamma phase consists of relatively large grains [9]. Small  $\text{Al}_2\text{O}_3$  inclusions located at the grain boundaries as well as numerous pull-outs and pores can be observed on the alloy surface due to the production by powder metallurgy. This very fine dispersion of defects may be detrimental for the macroscopic corrosion resistance of the gamma phase [9,10].

The samples were mechanically ground down to 4000 grit silicon carbide paper, polished with diamond paste in ethanol down to  $1\ \mu\text{m}$  and then ultrasonically cleaned in ethanol. The final rinsing was performed with isopropanol.

The samples were kept in a desiccator to keep the passive surface in a controlled reproducible low humidity atmosphere. Certain samples were exposed to controlled laboratory conditions ( $T=22.2\pm 0.2\ ^\circ\text{C}$  at  $35\pm 2\%$  relative humidity) for a duration between 30 min to 3 h to induce and determine the initial effect of air-aging on the passive layer formation and subsequent stability in acidic media.

Sulfuric acid at  $\text{pH } 0.0\pm 0.3$  and hydrochloric acid at  $\text{pH } 2.0\pm 0.3$  were used as electrolytes. The solutions were prepared respectively from suprapure sulfuric acid 96% and suprapure hydrochloric acid 30% (Merck, Germany) diluted with MilliQ water (Millipore, Switzerland,  $18\ \text{M}\Omega$ ,  $\text{TOC} < 3\ \text{ppb}$ ).

### 2.2. Flow microcapillary plasma mass spectrometry

The flow microcapillary plasma mass spectrometer setup (Fig. 1) is based on the coupling of a polypropylene microcapillary (epTips, Eppendorf, Switzerland) to a quadrupole ICPMS Elan 6000 (Perkin Elmer/Sciex, USA) via a FIAS 200 flow injection system (Perkin Elmer/Sciex, USA). As shown in Fig. 2, the flow injection system consists of two incorporated peristaltic pumps and an 8-port switching valve.

A microcapillary (inner diameter of  $520\pm 15\ \mu\text{m}$ ) is placed on the sample surface and filled with the chosen solution. The total volume within the microcapillary line (microcapillary+tubing) is  $450\ \mu\text{l}$ . Continuous circulation of the solution within the microcapillary line is ensured by a peristaltic pump (P2 in Fig. 2) at a flow rate of  $600\ \mu\text{l}\ \text{min}^{-1}$ .

The flow injection valve is initially in position 1 (Fig. 2a). In time intervals of 6 min over 120 min, the flow injection valve switches from position 1 to position 2 (injection position), sending the loop content ( $20\ \mu\text{l}$ ) to the ICPMS for element analysis (Fig. 2b). The loop is directly refilled with fresh solution to ensure a constant volume during the whole measurement time. The flow injection valve is then switched back to position 1 (Fig. 2c). During the

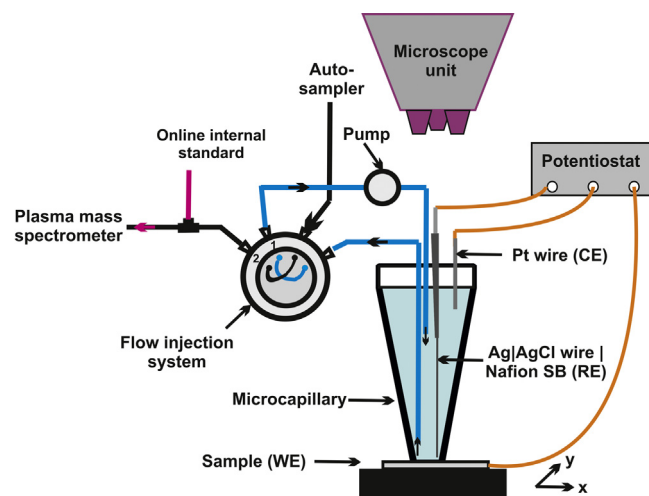


Fig. 1. Flow microcapillary plasma mass spectrometer setup.

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