# Study of the corrosion products formed on a multiphase CuAlBe alloy in a sodium chloride solution by micro-Raman and in situ AFM measurements

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## ARTICLE INFO

## ABSTRACT

The corrosion products formed on a multiphase Cu–11.40Al–0.55Be (wt.%) alloy in 3.5% NaCl at open circuit potential, and their evolution with immersion time were studied mainly by micro-Raman and in situ AFM measurements. The aluminium content of each phase affects the formation of the corrosion products on them. After 1 day of immersion, $\gamma_2$ precipitates were more susceptible to dealuminization, while $\alpha'$ phase exhibited a high corrosion stability. The corrosion products evolved with immersion time, and $CuCl_2$ and a $Cu_2O/CuO$ double layer film were the stable products formed on all the phases after long times.

## 1. Introduction

Cu–Al–Be system has been developed as a shape memory alloy (SMA) by adding small quantities of beryllium into eutectoid Cu–(11.4–11.8 wt.%)Al system, in order to decrease the martensitic transformation temperature and thereby obtain the pseudoelastic behaviour at room temperature [1–4]. These alloys are highly promising for applications as passive dampers of seismic energy in structural frames of buildings or in bridges [2,5].

The pseudoelastic behaviour can be modified, among other several factors, by the formation of precipitates [6]. Two types of precipitates can be observed in copper-based SMAs after aging treatments: $\alpha'$ phase in hypoeutectoid system and $\gamma_2$ phase in hypereutectoid system. For Cu–Al–Be alloys with an isothermal treatment between 400 and 490 °C, the formation of $\alpha'$ phase followed by the eutectoid decomposition ($\beta \rightarrow \alpha' + \gamma_2$) has been obtained [7].

Montecinos and Simison [8] studied the corrosion behaviour of $\beta$ and ($\beta + \gamma_2$) microstructures of a shape memory Cu–Al–Be alloy. Chloride-rich environments can produce dealuminization attack and the corrosion behaviour is affected by the alloy microstruc-

tural conditions. After long times of immersion, the single $\beta$ phase microstructure suffers localized corrosion in some regions but dealuminization is generalized on the whole surface. However, in the ($\beta + \gamma_2$) microstructure preferential dissolution of $\gamma_2$ dendritic precipitates occurs, which seems to protect $\beta$ matrix from de-alloying [8]. Han et al. [9] investigated the corrosion mechanism of a Cu–9Al–2Mn (wt.%) alloy, which exhibit a structure consisting of $\alpha$ and the eutectoid phase. They demonstrated that $\alpha$ phase did not show any change after 3 years of immersion in a marine environment, while the eutectoid structure suffered a preferential corrosion attack. Rosatto et al. [10] studied the electrochemical behaviour of Cu–Al–Ag alloys, and they found that $\gamma_1$ phase and the ($\gamma_1 + \alpha_1$) structure are the preferred attacked phases, while $\alpha_1$ phase would be the area where the cathodic reaction occurs.

The in situ tapping mode atomic force microscopy (AFM) has proven to be a very valuable tool for the analysis of thin films of oxides formed on metal surfaces and it provides quantitative measurements of the surface topography. In addition, this technique allows direct in situ measurements during the corrosion process taking place under controlled conditions [9,11]. Using this technique together with other ex situ measurements, which allows the identification of the corrosion products formed on the surface samples, it is possible to obtain a more accurate view of the evolution of the surface over time.

In situ AFM results of the first stages of corrosion of a multiphase shape memory Cu–Al–Be alloy in 3.5% NaCl are presented. The identification of the reaction products formed on each phase
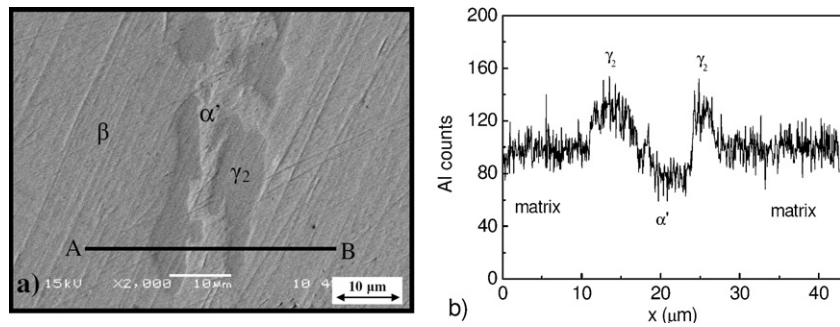
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**Fig. 1.** (a) Micrograph of a sample before the immersion (backscattered electrons-SEM); (b) aluminium compositional profile along the line A–B in Fig. 1a.

was done by ex situ micro-Raman measurements, jointly with other techniques, for immersion times in the range of 1–65 days.

## 2. Experimental procedure

The Cu–11.40Al–0.55Be (wt.%) polycrystalline alloy under study was obtained from Trefimetaux (France) as 15 mm diameter extruded bars. The chemical composition was determined by atomic absorption spectrophotometry. Prior to performing the heat treatment, the samples were previously heated during 5 min at 800 °C in the β field and water quenched at room temperature (single β phase microstructure). Precipitation of α′ phase was generated by an isothermal aging treatment at 505 °C, followed by water quenching at room temperature. A detailed description is given in [7]. The temperature was monitored using a chromel–alumel thermocouple. The software Image Tool 3.0 was used to estimate the volume fraction of precipitates in the specimens as the relative area occupied by them with respect to the total area. The samples were smoothed with 240, 600 and 1000 grit emery paper and then polished with alumina powder (0.3 μm size).

For corrosion tests specimens were immersed in a 3.5% NaCl solution adjusted to pH 8 with borate–boric acid buffer for different exposure times in the range of 1–65 days. The solution was maintained at room temperature (20 ± 2 °C) and air was bubbled through it. After the immersion, the samples surfaces were rinsed gently with distilled water, sprayed with ethanol and dried with hot air.

The surface morphology of the samples before and after immersion in the chloride solution was examined using an Olympus PMG3 optical microscope (OM) and a JEOL JSM-6460LV scanning electron microscopy (SEM). Energy dispersive X-ray spectroscopy (EDX) analysis under SEM was employed to obtain an estimation of the surface composition of different regions of the samples and their variability was obtained as the standard deviation of at least three experimental measurements. The beryllium content could not be detected by this technique. X-ray diffraction (XRD) using a PANanalytical X'Pert Pro PW3373 equipment with low incidence angle (3°) was used to identify the phase structure of specimens before the immersion and of the corrosion product films formed after that. It was operated at 40 kV and 40 mA with the excitation of CuKα (λ = 1.54056 Å).

Tapping mode atomic force microscopy (AFM) using an Agilent 5500 microscope was employed to study in situ the changes of the sample surfaces immersed in 3.5% NaCl adjusted to pH 8 during 21.5 h at open circuit potential.

Corrosion products after 1, 21 and 65 days of immersion at open circuit potential were locally characterized by micro-Raman spectroscopy (Invia Reflex confocal Raman Microprobe). The incident beam was focused on the specimens as a spot size diameter of 1 μm (high confocality mode). Excitation was provided with the 514 nm

emission line of an Ar⁺ laser and measurements were performed in backscattering configuration using a 50× objective.

## 3. Results and discussion

### 3.1. Microstructural characterization

α′ phase was formed in the samples by the isothermal aging treatment. Small quantities of γ₂ phase in some zones surrounding α′ were also obtained. A volume fraction of 1.2 ± 0.5% of α′ phase and 0.8 ± 0.6% of γ₂ phase was estimated from optical micrographs. The precipitates were difficult to distinguish on polished samples using the detector of secondary electrons in SEM. However, they could be observed by backscattered electrons, which provided information about the distribution of the alloying elements in the sample (Fig. 1a). The darker areas could be associated with a composition with lower atomic mass, which agree with EDX results (Table 1). Copper rich α′ phase (Table 1) was located mainly in the grain boundary zones. In some regions surrounding the α′ phase, dark precipitates, which correspond to γ₂ phase were distinguished (Fig. 1a and Table 1). Fig. 1b shows a compositional profile of aluminium along the line A–B in Fig. 1a. It can be clearly seen that α′ phase is poorer, while γ₂ phase is richer in aluminium than the matrix.

The XRD patterns of the samples before the immersion (Fig. 2b) confirmed the presence of γ₂ precipitates with a Cu₉Al₄ structure in a β DO₃ matrix and some β′ martensite phase. The presence
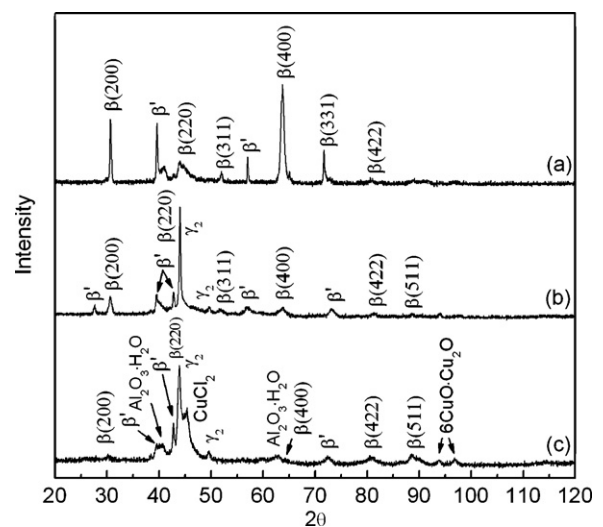


**Fig. 2.** XRD patterns of: (a) blank β sample; (b) (β + α′ + γ₂) sample before immersion; and (c) (β + α′ + γ₂) sample after 24 h of immersion in 3.5% NaCl. All the measurements were obtained at low incidence angle (3°).