



Scanning electrochemical microscopy to study the effect of crystallographic orientation on the electrochemical activity of pure copper



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ABSTRACT

The local electrochemical reactivity of high purity copper as a function of the grain orientation in the microstructure has been investigated. The different crystal orientations were determined by means of Electron backscatter diffraction (EBSD) followed by in-situ Scanning electrochemical microscopy (SECM) measurements operating in feedback mode across the very same copper surface. With this procedure it is possible to characterize in-situ the reactivity of selected grains in the polycrystalline microstructure of the copper. The study is focused on monitoring differences in the electrochemical response on $\langle 001 \rangle$ and $\langle 111 \rangle$ oriented grains. The behaviour of these selected orientations was studied under two surface conditions: passive state of copper after the formation of an anodic oxide layer, and corrosion or active state of the copper by immersion in chloride solution. In the case of the passivated copper it was observed that the grain with an orientation closer to $\langle 111 \rangle$ shows a lower reactivity compared to the grain where the orientation is nearer to $\langle 001 \rangle$, which confirmed that grain orientation has an influence on the electrochemical reactivity of the passive layer formed on the metal.

It was found that for the copper in the active state, the reactivity of a $\langle 111 \rangle$ oriented grain is higher when compared to a $\langle 001 \rangle$ oriented grain, which is contrary to the expected behaviour. This discrepancy could be explained by possible neighbouring effects between both grains.

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1. Introduction

Copper is a widely used metal mainly due to its good electrical and thermal conductivity. Therefore understanding the copper corrosion mechanism in different media has been the aim of a vast amount of literature in the last decades [1–5]. Corrosion studies have often been focused on macroscopic features, but recent literature indicates that the corrosion behaviour strongly depends on the local surface reactivity, and the surface reactivity itself can be strongly influenced by the crystallographic orientation [6–10]. In this respect, observations have shown that grains with $\langle 001 \rangle$ and $\langle 111 \rangle$ orientations have a significant influence on the corrosion behaviour of metals. For example, K. Lill, concluded that the critical current density on a grain with $\langle 100 \rangle$ orientation is 53% higher when compared to a $\langle 111 \rangle$ oriented grain in the

case of FeAlCr [11]. Studies of the initial stages of the oxidation of Cu(001) and Cu(111) have demonstrated that the atomic structure of the oxide is directly related to the grain orientation [12,13]. Additionally, differences in the duplex passive oxide layer morphology formed on Cu(111) and Cu(001) monocrystals have been observed [14]. Another interesting fact that we recently published goes further and confirms that not only does the grain orientation itself have an influence on the corrosion behaviour but also that the orientation of the neighbouring grains seem to play a decisive role on the dissolution rate of the metal [15]. Understanding the role of crystal orientation better on the initial stages of corrosion is a challenging topic, and requires precise knowledge of grain orientation on the metal microstructure and electrochemical techniques with the necessary high-resolution to monitor in-situ localized electrochemical activity related to crystallographic orientations. The Scanning electrochemical microscope (SECM) is a scanning technique that uses a microelectrode as a probe allowing in-situ characterization of the electrochemical processes taking place at a surface with submicron resolution. The SECM has been widely used to study the electrochemical activity and the local

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dissolution of different metals [16–22]. However works using this technique have scarcely been published on the study of electrochemical characteristics of grains and microstructural features on metals. K. Fushimi studied the growth of an oxide film on titanium and the electrochemical reactivity of this oxide depending on the crystallographic orientation of grains [22,23]. Nevertheless SECM measurements were carried out without previous knowledge of the surface microstructure which turns out to be one of the main drawbacks of this procedure. The use of different microelectrode techniques (including the SECM) with complementary EBSD analysis of the surface to study the corrosion of iron and Fe-7.5Al-7Cr and the influence of the grain orientation were discussed in a more recent review [24]. It was concluded that for alloyed iron, the dissolution was faster for the (001) single grain, while in pure iron the orientation that has a thicker passive layer or defect-free passive layer is also present on the (001) oriented grain. More recently B. Aaronson studied the reactivity of a polycrystalline platinum using scanning electrochemical cell microscopy (SECCM) which is a new generation of the conventional SECM. They showed that there is higher activity on grains with (101) orientation, compared to those with (001) and (111) [25].

This paper studies the grain dependent electrochemical reactivity of a polycrystalline copper, mostly focusing on $\langle 001 \rangle$ //ND and $\langle 111 \rangle$ //ND and close grain orientations. These orientations are identified by EBSD analysis of a polycrystalline area. Then SECM operating in feedback mode is used to monitor the electrochemical reactivity of the selected grain orientations for both a passivated and active copper surface in an in-situ manner. By the complementary use of surface analysis and local electrochemical measurement the effect of specific grain orientations on the reactivity of copper is established and more important, the effect of neighbouring grain orientation, on the local electrochemical behavior of pure copper.

2. Experimental

2.1. Sample preparation

The material used in this work was cast Electrolytic Tough Pitch (ETP-) Cu, obtained from Aurubis (Belgium). This material is a high purity cast copper, with no traces of sulfur and minimal amounts of oxygen. A warm rolling reduction was applied at 350 °C, which allowed changing the original cast microstructure into a newly recrystallized one. This was followed by an annealing treatment for 24 h at 800 °C in order to ensure full recrystallization and a suitable grain size for the spatial resolution of the SECM set-up employed in this work. The samples were mechanically grounded and polished, finishing with a 1 μm diamond paste. In order to be sure to characterize the same area of the samples, indents were made as markers and the same areas were characterized with both EBSD and SECM techniques.

2.2. Electron Backscatter Diffraction (EBSD)

Prior to the SECM measurements, the texture of the polycrystalline copper samples was characterized by EBSD [26]. To obtain a suitable surface preparation for EBSD, a final electropolishing step (10 V, 10 s) in a phosphoric acid electrolyte was necessary. The EBSD system was attached to an FEI field emission scanning microscope (FE-SEM) operated at 20 kV. Measurements were carried out with a step size of 0.5 μm and the orientation data was post-processed with the commercial orientation imaging software package OIM-TSL®. The orientation images were represented in this study as inverse pole figure (IPF) maps, i.e., the colour of each grain represents the crystal orientation that is parallel to the sample surface normal, commonly denominated as the sample ND direction.

2.3. SECM experimental setup and selection of the working mode

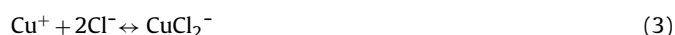
In order to choose the best working mode for the SECM measurements, a good knowledge of the corrosion process of copper is of pivotal importance. In pure water, Cu has a wide stability range but when chloride ions are present in the solution, the size of the stability zone decreases and also the area where soluble products are formed increases in size [27].

At present some ambiguity still exists about the initial electro-dissolution reactions of bare copper in neutral/acid chloride media. In their review G. Kear, B. Barker, and F. Walsh [28], summarized three possible mechanisms:

Mechanism 1



Mechanism 2



Mechanism 3



These reactions are all considered to be reversible and are assumed to be under mixed kinetics control close to the corrosion potential. Even though the exact path remains unresolved it is clear that two intermediate species cuprous chloride and/or cuprous ion may be involved in the initial reaction during the oxidation of copper to Cu^{2+} [29].

One of the possible operating modes to use the SECM is in the sample generation-tip collection mode. In this case, the microelectrode is used to monitor the flux of electroactive species generated at the surface. In our case, two possible species generated at the surface could be detected: Cu^+ and Cu^{2+} . The detection of Cu^{2+} by its electroreduction to Cu at the microelectrode would lead to the deposition of copper on the probe which is an undesired consequence. The detection of Cu^+ by its oxidation to Cu^{2+} at the microelectrode is theoretically possible although as cuprous ion is an intermediate specie of the corrosion mechanism, it is too unstable to be successfully detected by the SECM.

Another operating mode for SECM is the redox-competition mode in which the microelectrode competes with the substrate for the very same electrochemical specie [30]. This mode can be used to detect the depletion of oxygen in solution due to its consumption for the cathodic reaction at the copper surface during corrosion. In this case microelectrode and substrate “compete” for the available dissolved oxygen. However for Pt-microelectrodes the potential of oxygen reduction is in the range of reduction of Cu^{2+} to Cu.

Therefore this working mode was considered to be inappropriate to study our system.

The selected working mode was the feedback mode, using ferrocenemethanol as the electrochemical mediator. Operating in this mode makes it possible to distinguish between the different electrochemical reactivity on the surface. The oxidation of Fe(II) to Fe(III) of the electrochemical mediator is the selected reaction at the microelectrode. The tip current at the proximities of the metal surface is a function of the nature of the substrate, making it possible to distinguish insulating or conductive areas. In the case of an insulating surface, the current at the tip will be lower than the limiting current measured at the bulk of the solution. This in contrast to the proximities of an electroactive surface, for which the

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