Copper: A Model Alloy to Understand the Role of Microstructure in Sustainability

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Abstract

Metals are the materials pre-eminently used for structural applications. Since the use of metals is extremely versatile, they are exposed to an enormous diversity of environments. Often, this interaction has a detrimental influence on the mechanical, physical or esthetical properties. The degradation of the material properties, due to interaction with its environment, is often generally quoted as corrosion. Corrosion not only has a technological meaning and decreases the life span of metals, it also has important economical consequences and might even be responsible for accidents, sometimes even with fatal outcome. Consequently, a lot of money is spent on corrosion protection and the maintenance and replacement of products that fail or are contaminated as a result of corrosion. Moreover, corrosion also holds for a loss of raw material and energy.

In the pursuit of increasing the sustainability of metals, a thorough knowledge of the corrosion phenomenon is crucial. Nowadays, corrosion is often considered as a macroscopic phenomenon. On top of that, in scientific literature, emphasis is on compositional effects, which implies that the possible effect of microstructural characteristics is often overlooked. Recent research suggests an important correlation between grain size, grain orientation, grain boundary orientation and corrosion. The aim of this work is to obtain a better understanding of the relation between the corrosion behaviour and the microstructural characteristics. In this work, Electrolytic Tough Pitch (ETP) Cu is used as a starting material. By applying a warm rolling step, the original cast microstructure was modified. A thorough microstructural characterization via electron backscatter diffraction (EBSD) and some corrosion tests were performed. This should allow to give an indication on the link between grain orientation and grain boundary misorientation and differences in corrosion behavior.
1 Introduction

In our society, metals are used in all fields and applications, ranging from enormous constructions in buildings or aerospace, to very small units in electronic devices. The use of a specific metal or alloy can often be related to specific mechanical properties, for example when high strength combined with ductility is needed. In other cases, functional properties determine the choice for a specific metal, for instance in electronic devices, where a high electrical conductivity is required. Regardless of the application, there always is one common property present affecting the durability to a large extent, namely the fact that most metals interact with their environment, i.e. that they are electrochemically active in contact with an often aqueous environment. This property is reflected in the corrosion and passivation behavior or the reactivity during surface processing in general. The electrochemical behavior actually is a combined effect of two electrochemical features; the electrochemical potential as a thermodynamic property and the current density of the electrochemical reaction as a kinetic property. The driving force for an electrochemical reaction is a potential difference that results in a current flow from an anode to a cathode. So far, studies on corrosion have often focused on macroscopic features related to the chemical composition [1-4]. Microscopic features, such as crystallographic texture and orientation dependent electrochemical characteristics of polycrystalline metals received much less attention. Recent literature indicates a significant influence of the grain size on corrosion behavior [5] and with respect to the corrosion kinetics, an important influence of the microstructure was reported, resulting from two types of research. On the one hand, local studies on single crystals and on individual grains [6-9] and on the other hand, on the evaluation of individual grains in polycrystalline metals [10-16]. These studies mostly focus on the oxidation process as a function of the orientation of the crystal plane. A few quantify the differences between differently oriented grains. Lill et al. investigated the critical current density for the transition from active to passive behavior of a FeAlCr steel using cyclic voltammetry in a microcapillary cell [17]. Their conclusion was that the critical current density on the (111) plane is 53 % higher as compared to the (001) plane. There are also a number of fragmentary studies on the general electrochemical behavior of polycrystalline technical materials, mostly related to intergranular corrosion. These studies study the phenomenon as a function of the specific alloying elements and precipitates present [18-20], the influence of thermomechanical processing [21-23] or grain boundary engineering [24-26]. Additionally, there are a few studies on pure bi-crystals. On the (100) and (111) iron plane the difference in current density is measured [14]. This experiment shows that the corrosion tendency is highest on the most closely packed (111) plane. The active dissolution peak of the (111) plane has a maximum current density of 6.7 mA cm⁻². Conversely, the maximum current density of the active dissolution peak of the (100) plane is only 1.25 mA cm⁻². In a Cu bi-crystal, the misorientation between grains is reported to affect the anodic/cathodic nature of the grains versus the grain boundaries [27]. Miyamoto et al. state that there is a critical misorientation angle between 70.5 ° and 105 ° that determines if the grain or the grain boundary will be attacked or not. All these studies demonstrate that the local, microscopic features influence the electrochemical behavior, but a physically founded relationship is still lacking. The present work describes an onset of a study that aims...
to quantify the local electrochemical behavior by systematically linking it to the microstructural variables. In the next section, the corresponding general strategy will be discussed in more detail before presenting the first experimental details and results.

2 Aim

2.1 General strategy

In analogy with mechanical engineering, where the bulk microstructural features of the metal are related to its mechanical properties, this study aims to link the electrochemical behavior to the microstructural characteristics of the metal surface. Unfortunately, electrochemistry has the disadvantage that there is no electrochemical equivalent to the material models such as those that link the macroscopic mechanical behavior to the microscopic crystal plasticity in mechanics. In order to deal with this lack of models, a first step is a systematic approach, which, on the one hand, consists of a controlled variation and thorough quantification of the microstructure and, on the other hand, meticulous quantification of the resulting electrochemical behavior.

2.2 Choice of the model system

Except for single crystals, metals consist of many grains with different crystallographic orientations. At first, we need a relatively simple model system of which the microstructure can be controlled. Related literature studies are often on metals such as stainless steel, aluminum and titanium which are covered by a native oxide film. This film dominates the electrochemical response and thus complicates the interpretation and correlation with the underlying metal microstructure. To circumvent this problem, Electrolytic Tough Pitch (ETP) copper will be used as a model system. Copper can be obtained with a high purity and the nm-thin surface oxide film does not disturb the electrochemical behavior to such an extent as for certain other metals. It is also possible to remove this oxide film [28]. Another important reason why copper is chosen as a model system is of its low stacking fault energy. As a result of this, copper is a metal that shows abundant annealing twinning when exposed to a thermomechanical treatment. This means that it is possible to control the population of specific grain boundary types in the microstructure by deforming the material by a crucial amount and applying specific heat treatments [29-31].

2.3 Variation and evaluation of the microstructure

For the chosen material, the microstructure will be varied by thermomechanical processing, which includes hot rolling, cold rolling and annealing. Grain size, crystallographic texture and grain boundary orientation can be controlled to a certain extent by varying the deformation and annealing parameters. In particular, the aim is to increase the proportion of so called “special boundaries”, where special boundaries are those whose close-fitting interfacial geometry leads to improved properties [25, 27, 32-34]. This was termed “grain boundary design and control” by Watanabe, but now has
evolved to the concept of grain boundary engineering (GBE) [35]. Grain boundaries can be characterized within the coincident site lattice (CSL) concept [36]. CSL boundaries are represented by a $\Sigma n$ value, with $1/n$ being the fraction of lattice points belonging to the coincident lattice. In case of for example $\Sigma 5$ one out of five lattice sites is common across the grain boundary. For low values of $\Sigma n$ the grain boundary is believed to have better corrosion resistance than boundaries with higher $\Sigma$ values. Consequently, to evaluate the corrosion behavior, the amount of low value $\Sigma n$’s in copper will be varied as much as possible.

To evaluate the microstructural characteristics of the metal, electron backscatter diffraction (EBSD), a technique that can be attached to a scanning electron microscope, will be used. Apart from the texture and microstructure analysis, surface topology visualization is performed by making use of atomic force microscope (AFM). This technique makes it possible to quantify the surface roughness, or in the particular case of this work; the height differences between different grains and grain boundaries after corrosion has taken place.

2.4 Quantification of the electrochemical behavior

The electrochemical behavior that is observed on the metal on a macroscopic scale is the convolution of the individual contributions of local electrochemical processes. Thus, in order to understand the general electrochemical behavior, it is obligatory to study the local electrochemistry. This feature is closely related to local microstructural elements. Consequently, the general and local electrochemical properties will be measured as a function of the microstructural variables. The aim is to determine both general and local electrochemical potential differences, the electrochemical currents and their distributions across the metal surface, linked to the anodic/cathodic surface activity distribution of the metal. The electrochemical study will be performed in NaCl solutions where local intergranular corrosion is induced. Macroscopic electrochemical properties are measured using classical electrochemical polarization experiments. With the Scanning Kelvin Probe (SKP) the Volta potential distribution in the metal surface is measured with a high lateral resolution of about 1 nm [37-39]. This means that anodic and cathodic sites in the microstructure can be identified. Furthermore, the Scanning Vibrating Electrode Technique (SVET) will be used to measure the local current densities with a lateral resolution of 20 $\mu$m [40]. The SVET is used to map the distributions of ionic currents in a plane directly above the surface. The technique is useful to identify zones of anodic and cathodic activity, as well as observing changes in activity as a function of time. SVET provides a promising method to characterize in-situ the micro-electrochemical activities at grain boundaries and in particular grains [41].
3 Experimental procedures

3.1 Thermomechanical processing

The material used was cast Electrolytic Tough Pitch (ETP) copper, obtained from Aurubis (Belgium). A warm rolling reduction of 75 % at 350 °C was applied by using lab facilities available at Ghent University and allowed destroying the cast microstructure and provided a completely recrystallized microstructure. Subsequently, the samples were prepared for microstructural investigation by mechanical grinding and polishing, finishing with 1 µm diamond paste. To have a suitable surface finish for EBSD, a final electropolishing step (10 V, 10 s) in a phosphoric acid electrolyte (D2 from Struers®) was necessary. The EBSD system is attached to an FEI® environmental scanning electron microscope (ESEM XL30) with a LaB₆ filament operated at 20 kV. Step sizes were varied between 0.5 µm and 20 µm taking into account the evolution of the grain size for the different annealing treatments. The inverse pole figure maps (IPF), grain size and grain boundary misorientation were calculated and analyzed by the commercial orientation imaging (OIM)-TSL® software. The accuracy of a misorientation measurement obtained by EBSD is 0.5 °. The Brandon criterion for allowable angular deviation [42] was used to determine the CSL boundary fraction as a fraction of total boundary length. In particular this was done for the Σ3 and Σ9 grain boundaries, allowing an angular deviation of 8 ° and 5 °, respectively.

3.2 Corrosion

After electropolishing, the cast and a warm rolled Cu samples were rinsed with deionized water and degreased with acetone. Finally, they were submerged in a 0.5 M NaCl solution for 3 h to induce grain boundary corrosion. On these two samples, a scanning electron micrograph (SEM) was taken and EBSD was performed on one and the same place. Subsequently, also other corrosion experiments were conducted. The warm rolled Cu was polished, finishing with 1 µm diamond paste. After rinsing with deionized water and degreasing with acetone, the samples were submerged for 90 min and 150 min in 0.1 M NaCl, respectively. Finally, the samples were electropolished according to the same procedures as mentioned above.

4 Results and discussion

4.1 Thermomechanical processing

Figure 1 shows the inverse pole figure (IPF) map of the as-cast ETP-Cu. The legend on the right hand side provides an indication of the corresponding crystallographic orientation. The IPF map shows that the as-cast Cu has a quite random texture, i.e. no preferential texture components were observed. The average grain size is 343 µm, but a reasonable amount of scatter is observed. When looking at the grain boundary map (Figure 1) only 0.3 % of the boundaries are Σ3 or Σ9. In order to wipe out the features of the as-cast microstructure, a warm rolling was performed.
Figure 1: IPF map and grain boundary map of the as-cast ETP-Cu. Random boundaries are indicated as thin grey lines, $\Sigma 3$ boundaries as thick black lines and $\Sigma 9$ boundaries as thick grey lines.

Figure 2: IPF map and grain boundary map of warm rolled ETP-Cu (left). Random boundaries are indicated as thin grey lines, $\Sigma 3$ boundaries as thick black lines and $\Sigma 9$ boundaries as thick grey lines. ODF, reconstructed from the crystallographic orientations of 3877 grains. Levels: 1.0 – 1.4 – 2.0 (right).

After warm rolling the ETP-Cu has a completely different microstructure (Figure 2). It still has a quite random texture, but when looking at the grain boundaries, more CSL boundaries are identified. The randomness of the texture is illustrated by means of the ODF. This ODF is reconstructed.
from the crystallographic orientations of 3877 grains of the warm rolled ETP-Cu. The maximum intensity was found to be about 2.5 times random. The ETP-Cu has an average grain size of 6 µm and 53 % are either $\Sigma 3$ or $\Sigma 9$ boundaries.

4.2 Corrosion

Figure 3 shows the result of the corrosion experiment that was conducted on the as-cast ETP-Cu sample. The SEM image clearly shows that immersing the as-cast sample for 3 h in 0.5 M NaCl causes grain boundary corrosion. All boundaries are equally attacked, but this was expected as no CSL-type of boundaries is present in the as-cast microstructure. The orientation of the four different grains is shown in the IPF map. This figures shows that the combination of EBSD and SEM can be a powerful tool in understanding grain boundary corrosion.

![Figure 3: IPF map (left) and corresponding SEM image (right) of grain boundary corrosion in the as-cast ETP-Cu immersed in 0.5 M NaCl for 3 h at RT](image)

When conducting the same experiment on the warm rolled ETP-Cu sample, a completely different corrosion behavior can be observed (Figure 4). This immersion not only causes grain boundary attack, but also extensive pitting is observed. Pitting is a local phenomenon that is related with the presence of the thin oxide layer and is initiated at some weak spots in this layer. Apparently, applying a warm rolling step affects to some extent the protective properties of ETP-Cu oxide film. Field Emission Auger Electron Spectroscopy (FE-AES) and X-ray Photoelectron Spectroscopy (XPS) will be conducted to reveal the reason for the observed pitting. Still, when looking at the SEM
image of the corroded warm rolled sample (Figure 4), it can be seen that CSL boundaries are less severely attacked. To quantify and compare the amount of attack of the different types of boundaries AFM measurements have to be conducted. Also, a Kelvin probe can be coupled to the AFM (SKP-AFM), which will make it possible to map the Volta potential distribution. In this way, it will be possible to quantify the anodic/cathodic nature of the different types of grain boundaries. To confirm the outcome of these results, SVET measurements will be conducted. SVET allows to map the distributions of ionic currents in a plane directly above the surface. In that way, it becomes possible to characterize in-situ the micro-electrochemical activity at the grain boundaries.

Figure 4: IPF and image quality map (left up), corresponding grain boundary map (left down) and SEM image (right) of a corroded warm rolled ETP-Cu sample, immersed for 3 h in 0.5 M NaCl. Random boundaries are indicated as thin grey lines, $\Sigma 3$ boundaries as thick black lines and $\Sigma 9$ boundaries as thick grey lines.

To circumvent the problem of pitting and to focus on the grain boundary corrosion a corrosive environment that only attacks the grain boundaries in the thermomechanical processed samples is required. The use of 0.1 M NaCl gives satisfying results (Figure 5). Immersion of the warm rolled sample for 90 min in this solution causes preferential attack of some grain boundaries. It is assumed that this can be linked to the different types of grain boundaries. When immersing the sample for 150 min all boundaries show corrosion, but already from the SEM image it is seen that some boundaries suffer from more severe corrosion than others. Further investigation with the above
mentioned techniques will allow to further distinguish between the grain boundary character and the electrochemical properties of it.

Figure 5: SEM images of a corroded warm rolled ETP-Cu sample immersed for 90 min (left) and 150 min (right) in 0.1 M NaCl

5 Conclusion

The present data are some preliminary results of the study to increase a sustainable use of metals by a thorough knowledge of the corrosion phenomenon. It was shown that it is possible to conduct EBSD and SEM on the same place in order to identify differences in corrosion for different types of grain boundaries. The first step was to find a suitable corrosive environment to induce grain boundary corrosion and to illustrate the different corrosion behavior of different grain boundaries. The present results nicely illustrated that this was possible. The next step will be to further quantify the electrochemical behavior of the different microstructural elements by AFM, SKP and SVET.

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