Investigations on Anode Quality in Copper Electrorefining

Article *in* BHM Berg- und Hüttenmännische Monatshefte · March 2008

DOI: 10.1007/s00501-008-0356-7

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Investigations on Anode Quality in Copper Electrorefining

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Copper anodes have to have a certain quality in order to meet the requirements of subsequent electrorefining. The anode casting process is decisive for anode quality, which determines anodic dissolution behaviour during electrorefining. In order to determine the influences of the casting process and cooling conditions on chemical and physical anode quality, the anode casting process at Montanwerke Brixlegg AG and corresponding anode samples were investigated thoroughly. Temperature measurements in the anode moulds pointed out the influence of the process parameters mould material, mould wash, mould life, and cooling. The investigated anodes demonstrated a relatively homogeneous elemental distribution, as well as type and distribution of inclusions, which led to a focus on physical quality. The effects of the varying physical quality over anode thickness on electrorefining were studied with potential measurements that showed differences in dissolution behaviour for the different structures and grain sizes, respectively.

Untersuchungen zur Optimierung der Anodenqualität in der Kupferraffinationselektrolyse. Kupferanoden benötigen eine gewisse Qualität um den Anforderungen der nachfolgenden Raffinationselektrolyse gerecht zu werden. Der Anodengießprozess hat große Bedeutung für die Anodenqualität, welche wiederum das anodische Auflösungsverhalten bei der Raffinationselektrolyse bestimmt. Um die Einflüsse des Gießprozesses bzw. der Abkühlungsbedingungen auf die chemische und physikalische Anodenqualität abzuklären, wurden der Gießprozess bei der Montanwerke Brixlegg AG und die entsprechenden Anodenproben untersucht. Temperaturmessungen in den Gießformen zeigten den Einfluss der Prozessparameter Formenmaterial, Schlichte, Einsatzdauer der Gießform und Kühlung. Die untersuchten Anoden zeigten eine relativ homogene Elementverteilung sowie einheitliche Art und Verteilung der Einschlüsse, was zu einer Fokussierung auf die physikalische Qualität führte. Die Auswirkungen der variierenden physikalischen Qualität über die Anodendicke auf die Raffinationselektrolyse wurden mithilfe von Potenzialmessungen untersucht, welche Unterschiede im Auflösungsverhalten für die unterschiedlichen Strukturen bzw. Korngrößen zeigten.

1. Introduction

Copper refining is necessary for impurity removal in order to achieve the properties desired by the customers. The refining is done in two steps: firstly, anode copper is produced by fire refining in an anode furnace and then cast into anodes. These are subjected to electrorefining, the second refining step.

Anode casting, which is the link between pyro- and hydrometallurgy of copper, has a wide influence on both chemical and physical anode quality, and hence determines anodic dissolution and electrorefining operations (output/efficiency, quality), respectively. As can be seen in Fig. 1, the optimization of electrorefining consists of two steps. Firstly, an increase in current efficiency would lead to a more homogeneous current density distribution in the whole tankhouse, as symbolized by the transition from the broad curve to the narrow one. If this first step

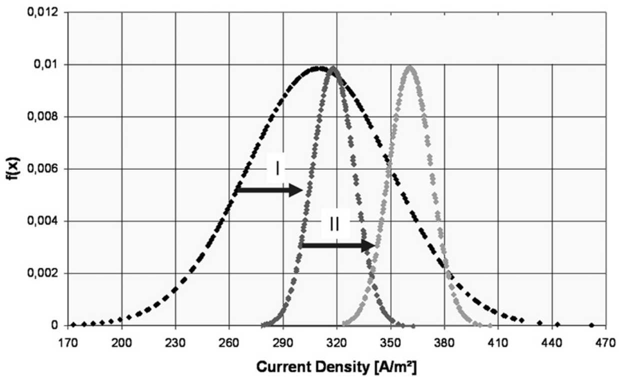

Fig. 1: Optimization potential in electrorefining (Gaussian bell curve)

can be realized, than also the second step becomes possible, which is increasing the current density, e.g. by optimizing the anode quality and the casting process.

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2. Anode Casting Process and its Influence on Anode Quality

The anode has to have a certain physical and chemical quality in order to meet the requirements of electrorefining, i.e. to achieve a high current efficiency, low energy consumption, low amount of anode scrap together with high cathode quality[1]. To satisfy the requirements of the electrolysis the anodes must provide uniform corrosion, weight, and geometric dimensions (especially thickness), smooth surfaces, minimal edge effects as well as minimal distortion of the body and the lugs. Uniform anode weight and therefore thickness as well as smooth surfaces are essential for uniform anode spacing and hence dissolution. Nonperfect vertical anodes cause much more pronounced effects during electrorefining than other anode properties, e.g. structure[2].

Chemical quality criteria are minimum content of harmful impurities, surface conditions of anode body (especially absence of passivating films), density, and gas-saturation capacity[3]. The chemical quality is mainly the task of fire refining, but it can also be influenced during the casting process, due to oxygen uptake during casting, slag carry-over from the anode furnace, and metal/refractory interactions.

Anode quality is not only dependent on the casting technology used, but especially on proper process control[3]. The most common technique is anode casting on casting wheels[4], although it is linked with certain disadvantages compared to continuous casting of copper anodes, especially regarding geometrical accuracy and surface quality[1,3–6]. Anode casting in vertical moulds with and without cooling was only investigated on laboratory scale[3].

The structure of the anode, which is linked with the elemental distribution and dependent on both thermodynamic and kinetic parameters, has an influence on the dissolution behaviour [5]. The solidification type is of special importance in secondary metallurgy as – due to varying scrap compositions – the impurity contents are much higher and hence have a wide influence on electrochemical behaviour of the anodes. During solidification some elements are enriched in the solid phase (e.g. Ni), others in the melt (e.g. As, Sb, Bi). This leads to either solid solutions or separate phases of various compositions in the solidified anode. The most inhomogeneous distribution causes different dissolution rates when contacting the electrolyte[5].

Casting wheel anodes have a typical cast structure. Due to the different cooling conditions from airside to mouldside, the following zones are found[5,7,8]:

- mouldside: thin zone with fine grains (ca. 1 to 2 mm)
- towards centre: columnar crystals, up to 5 mm long (area 3)
- centre: last solidified part with high amount of seeds – very fine globulitic structure (area 2)
- airside: solidified in contact with the atmosphere (air), usually cooled with water spray cooling – equiaxed, coarse grains (area 1)

The dissolution rates and the necessary energy for dissolution, as well as the tendency for passivation are different for the mentioned anodic areas[7]. As – due to the lower (crystallization) overvoltage – electrochemical dissolution occurs preferentially at the copper grain boundaries, the grain size distribution has an influence on anodic dissolution: anodes with finer grains dissolve more rapidly because of their higher content of grain boundaries[5]. However, anodes with finer grains are more susceptible to passivation, so that – regarding passivation – a uniform, relatively coarse, equiaxed structure is desirable[7]. As anodes with globulitic structures are less susceptible to passivation, the dissolution behaviour of anodes could be improved by magnetic stirring, which minimizes the dendritic zone and results in a smoother transition zone between dendritic and inner globulitic zone[5].

Not only the grain size, i.e. the macrostructure, but also the secondary dendrite arm spacing (DAS), i.e. the microstructure, is influenced by the cooling conditions[9]. The literature statements concerning influence of grain size and DAS on passivation behaviour are not consistent[7,10,11].

Due to their different dissolution behaviour, the anodic structures (as well as anode/cathode spacing) would request different cathodic crops. An optimum schedule would be as follows: In the 1st – shorter – period, the anodes are thick and the structural differences between air and mould side significant (dissolution of areas 1 and 3). As the irregular outer areas of the anode are dissolved, anodic dissolution improves (dissolution of area 2), which results in a longer 2nd period. This is followed by an – again – shorter 3rd period that deals with irregular shaped, maybe porous and perforated anodes, which cause irregular current densities, and therefore irregular dissolution (which leads to copper losses to the anode slime) and deposition.

The structure and elemental distribution can be influenced by solidification conditions, e.g. cooling rate and heat transfer, and these in turn by:

- mould material (thermal conductivity)
- mould wash
- amount of cooling water
- mould preheating
- thermal treatment of anodes
- casting temperature of liquid anode copper

Smooth anode surface as well as uniform anode weight and thickness are dependent on proper control of the casting process and the weighing system, respectively.

A more detailed description of the importance of chemical and physical anode quality regarding dissolution during electrorefining as well as possibilities for influencing is given in[12,13].

3. Experimental

The investigated anodes were produced on a 14-mould casting wheel at Montanwerke Brixlegg AG, a secondary copper producer in Austria. A temperature measurement system was installed in the anode moulds in order to determine the temperatures in the mould and deduce the cooling conditions of the anodes. The moulds were drilled and thermocouples positioned at 4 defined positions in 4 depths (surface, 50/100/140 mm). Furthermore, the temperature and the amount of the cooling water used for water spray cooling were measured. Samples were taken from the corresponding anodes. A variation of process parameters (Tab. 1) was carried out in order to determine their influence on the cooling conditions of the anode. As a further variation, moulds with cooling ribs at the bottom were studied.

Samples were cut from the corresponding anodes and prepared for analysis of chemical and physical quality. In order to study inhomogeneities over anode thickness, the samples were cut into slices (Fig. 2).

The chemical analysis was carried out with spark emission spectroscopy (at least 3 measurements per slice) and quantitative Scanning Electron Microscopy

Table 1: Variation of process parameters

anode	mould material	mould wash
A	anode copper	barite
B	anode copper	barite
C	cathode copper	barite
D	anode copper	barite
E	anode copper	carbon black
F	cathode copper	barite
G	anode copper + cooling ribs	barite

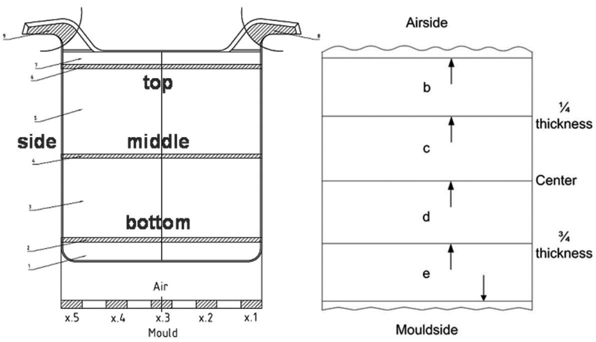


Fig. 2: Samples for investigation of inhomogeneities over anode thickness

(SEM). SEM was also used to study the inclusions more in detail.

For the investigation of micro- and macrostructure, the samples were ground, polished, and etched with ammoniumpersulfate solution with different concentrations. The image analysis software Clemex Nikon was used to study the different grain sizes and secondary dendrite arm spacing (DAS).

Anodic polarization scans at embedded samples (10 × 10 mm) contacted with an insulated copper wire, ground, and cleaned before starting the measurement were done at a scan rate of 0.1 mV/s. In order to keep the experimental conditions and the distances between the electrodes constant, a sample holder made of PTFE was used. Each experiment was repeated twice for reproducibility. The electrolyte composition (50 g/l Cu, 20 g/l Ni, 175 g/l H_2SO_4) was chosen close to the composition at Montanwerke Brixlegg AG. The experiments were

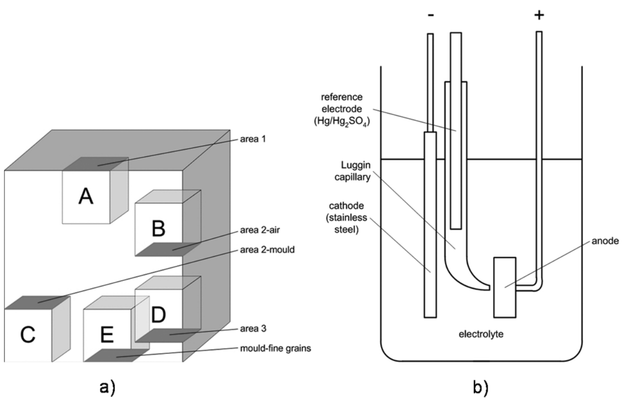


Fig. 3: Samples (a) and experimental setup (b) for potential measurements

carried out with an electrolyte volume of 700 ml at a temperature of 65 °C.

Positions of specimens in the anode are shown in Fig. 3 a). Experimental setup is shown in Fig. 3 b). As reference electrode served a mercury/mercury sulfate electrode at a potential of 650 mV_{SHE} (SHE…standard hydrogen electrode). All potentials are given with respect to the mercury/mercury sulfate electrode.

Before starting the anodic scan the open circuit potential (OCP) was measured for 5 min, which was sufficient since OCP reached a rather constant value within this time.

4. Results

4.1 Chemical quality

The chemical composition of the anode copper during casting was analysed every hour in order to investigate compositional variations within one batch (Fig. 4). The implementation of gas purging in the anode furnace ensures a constant composition of the anode copper during casting. The reported varying metal composition (e.g. variations of Pb and Ni content of up to 30 % and 20 %, respectively[14]) between the first and last amounts of molten copper poured from the anode furnace was not found.

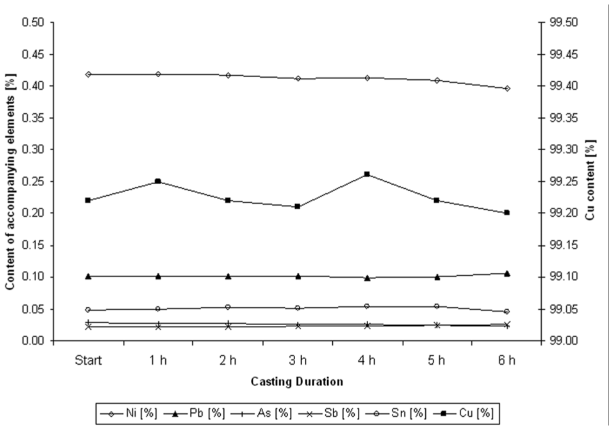


Fig. 4: Variation of chemical composition during casting

The elemental distribution over anode thickness for different cooling conditions is shown in Fig. 5. The dotted lines represent the average analysis, the solid lines the mean value of the chemical analysis of each slice. Unlike in literature statements[2,5], which describe a significant uneven elemental distribution due to the different distribution coefficients of the elements, a relatively homogeneous composition over anode thickness was found, independent of the mould material used. This could be due to the fast cooling of the anodes at Montanwerke Brixlegg AG. The use of carbon black as mould wash (Fig. 5, 6) resulted in even smaller deviations of the chemical composition over anode thickness. No definite trend for the general behaviour of the different elements was found.

Over anode area no big differences in chemical composition were detected either (Fig. 6).

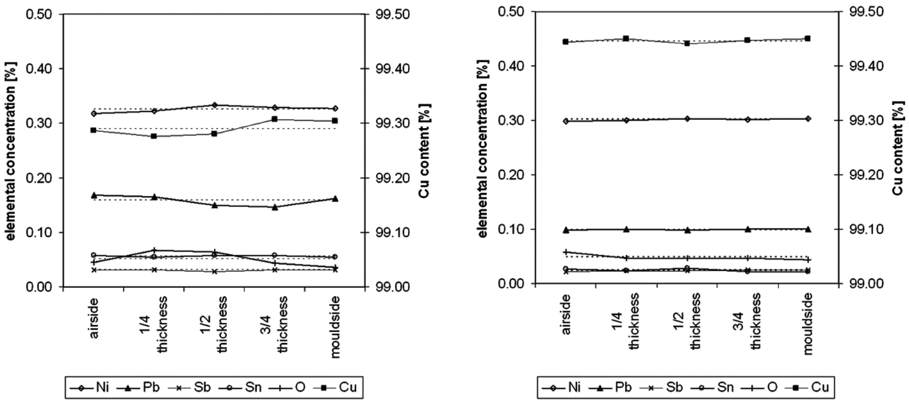


Fig. 5: Elemental distribution in anode B (left) and anode E (right)

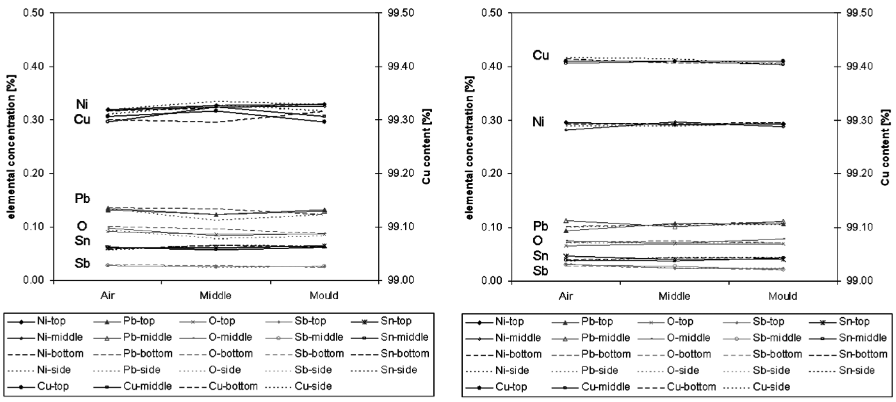


Fig. 6: Elemental distribution over anode area in anode D (left) and E (right)

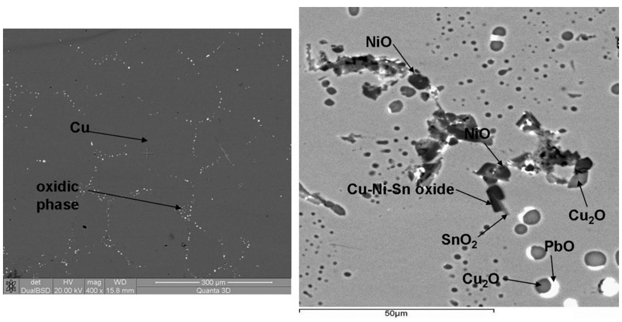


Fig. 7: SEM investigations (anode A, bottom, airside)

The structure was found to consist of primary Cu dendrites and a eutectic phase (Cu-Cu_2O). The oxidic particles do not only consist of Cu and O, but also contain a certain content of other accompanying elements (Ni, Pb, Sn), as described by[6,14,15]. The Cu_2O particles are often partially rimmed with PbO (Fig. 7). The types of detected phases were generally the same on airside and mouldside and agree very well with previous studies[6,15,16].

Besides these relative small spherical particles (some µm) also some larger „inclusions" were found, which seem to be gas inclusions trapped during solidification. Various oxides, containing Sn, Zn, Ni, As, Sb, Pb, and Fe have formed in these areas. These pores are also visible without a microscope and appear as black spots under the microscope.

As no definite variations concerning chemical anode quality were found over anode thickness, although the

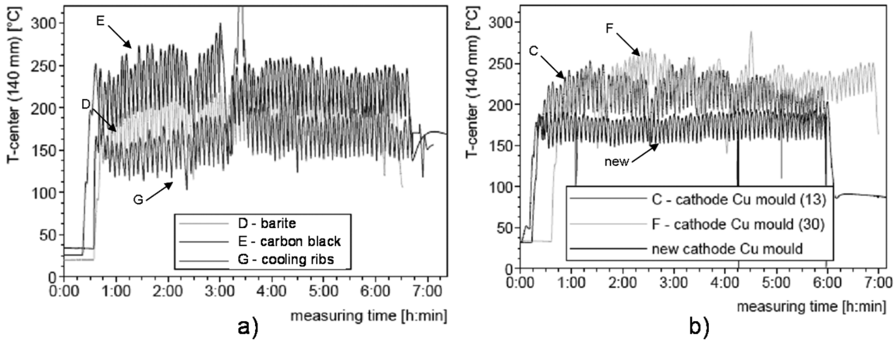


Fig. 8: Mould temperature as a function of different cooling conditions (a) variation of mould material and mould wash, b) different number of casting days

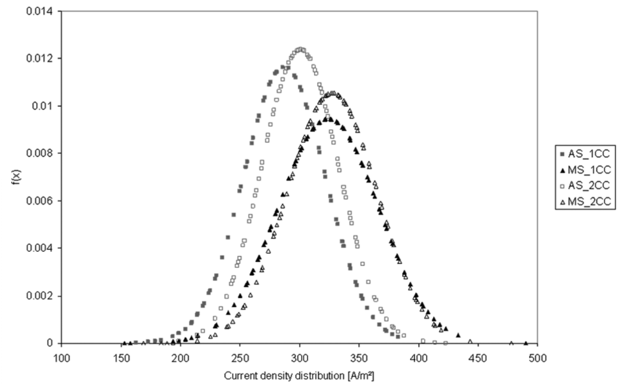


Fig. 9: Current density distribution in electrorefining (Gaussian bell curve)

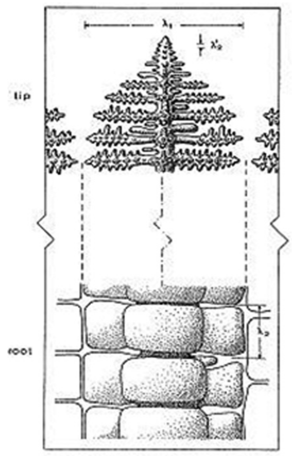


Fig. 11: Growing dendrite tip und dendrite root in a columnar structure[9]

mould temperatures and cooling conditions during anode casting were different (Fig. 8), the different behaviour of airside (AS) and mouldside (MS) during electrorefining (Fig. 9) is considered to be caused mainly by inhomogeneous physical quality, i.e. structure. If the different behaviour were caused by variations in chemical quality, which should occur only in the outer zones of the anode and hence have an effect in the first cathodic crop (1CC), then there should not be a difference between airside and mouldside in the second cathodic crop (2CC), as the outer regions are already dissolved.

4.2 Physical quality

The zones with different structures as described in literature were found in all anode samples where barite was used as mould wash. Also the inner region (area 2) shows a certain variation in grain size and was hence divided into area 2-air and area 2-mould for the investigations.

Unlike the other investigated anodes, anode E had a relative homogeneous and globulitic structure. This may be caused by a smaller temperature gradient due to the higher mould temperatures when using carbon black (see also Fig. 8), which was applied with an acetylene burner, and hence had the same effect as mould preheating.

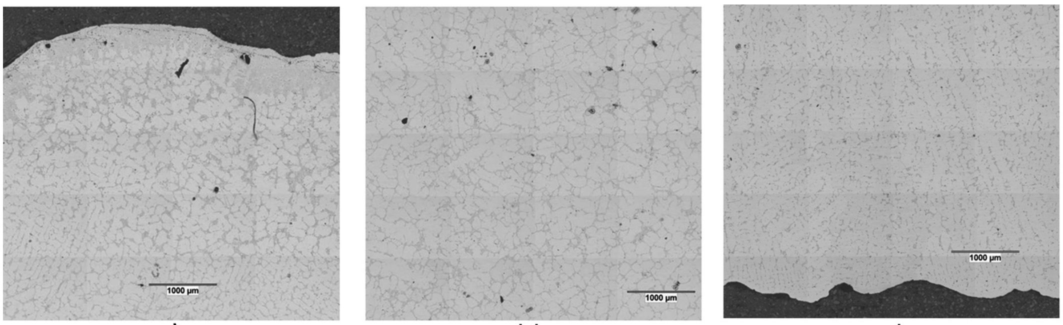
The different solidification conditions over anode thickness can be seen from the variation in secondary dendrite arm spacing (DAS, λ_2) (Fig. 10). Unlike the characteristic trunk spacing λ_1, that has the same value in the solidified microstructure as during growth, λ_2 undergoes a ripening process and increases enormously with time (Fig. 11). Hence, the value of λ_2 gives an indication of the local solidification conditions.

4.3 Anodic Dissolution

These experiments study the whole influence of the anode on dissolution behaviour and electrorefining, respectively, as all influences, i.e. chemical and structural properties, are included. The dissolution of an anode with a defined chemical composition and known structure is investigated.

As the chemical composition within the anode sample was found to be relatively constant over anode thickness, the samples were chosen according to the different solidification structures. The potential measurements were carried out with samples from anode C (position see Fig. 3 a).

Anodic polarization scans on samples with different structures show some differences in dissolution behaviour over anode thickness (Fig.12). The dissolution behaviour can be characterized by the maximum current density at which passivation occurs (i_{max}) at the so-called Flade-Potential (E_F). As anodes with a lower E_F, i.e. a less noble behaviour, are dissolved more readily, a high i_{max} at a minimum E_F would be desirable. The observed values for i_{max} and E_F of the different samples are listed in Table 2. According to these values and the curves in Fig. 12, respectively, anodes like the samples A and C, representing a not too fine equiaxed structure, would be preferable regarding E_F and i_{max}. In order to produce such a structure throughout the anode, very high cooling rates would be necessary both on mould and air side, or a smaller temperature gradient, i.e. a higher mould temperature, as in anode E.



a) b) c)

Fig. 10: Microstructure on airside (a), centre (b), and mouldside (c)

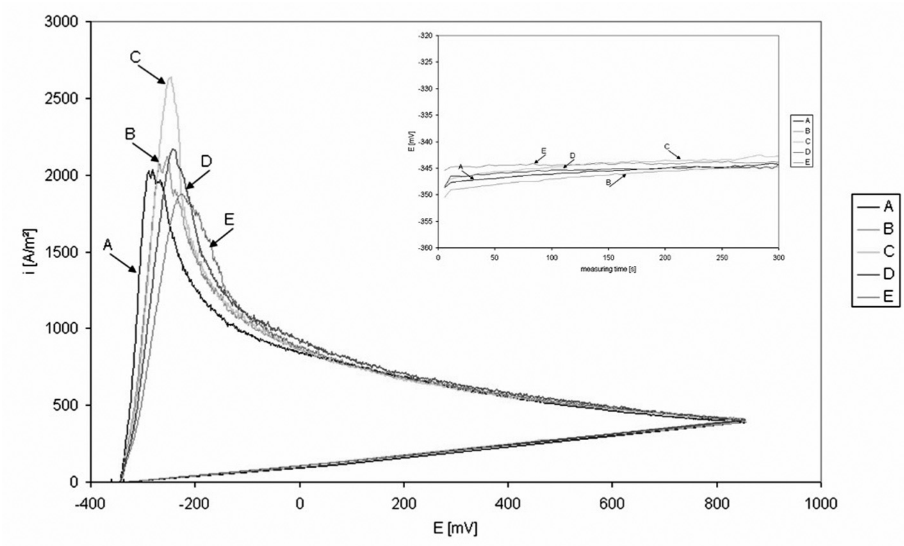


Fig. 12: Current density potential curves for samples over anode thickness

Table 2: Results for samples over anode thickness

Sample	structure	E_F [mV]	i_{max} [A/m²]	Open Circuit Pot. [mV]
A	outer equiaxed	-283	2427	-345
B	inner equiaxed	-252	2433	-346
C	inner equiaxed	-246	2785	-344
D	columnar	-242	2188	-345
E	fine equiaxed	-215	2044	-344

5. Summary and Outlook

Secondary copper anodes were thoroughly investigated for chemical and physical quality. A relatively homogeneous chemical quality was detected in all investigated samples, no definitive general trends for elemental distribution were found. Hence, the physical quality, i.e. grain structure and orientation, seems to have a major influence on uneven anodic dissolution during electrorefining. The physical quality can be influenced by the cooling conditions of the anode and the casting process, respectively. Proper control of the casting process and the weighing system, respectively, ensures smooth anode surface as well as uniform anode weight and thickness.

The investigations of dissolution behaviour showed variations over anode thickness. A not too fine equiaxed structure seems preferable for electrorefining.

6. References

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