Investigations on anode casting wheels to optimise anode quality

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Abstract

Anode casting is the link between copper pyro- and hydrometallurgy. To achieve good electrorefining performance, the anodes must have a certain chemical and physical quality. The latter is directly linked with the anode casting process.

The anode cooling and solidification conditions were determined from mould temperature measurements. To investigate the influence of the casting process on solidification, cooling conditions, and anode quality, the process parameters mould material and mould wash were varied. The use of different mould materials and mould wash, as well as the moulds' different number of days in use, resulted in significant differences in mould temperature and hence anode cooling conditions. However, these temperature variations did not seem to have an influence on chemical anode quality, but on physical quality. Variations in structure were detected in the different anodes, namely across the anode thickness and over the anode area, which indicated different local cooling conditions.

As there were no differences across the anode thickness due to chemical quality, the inhomogeneous anodic dissolution behaviour might be caused to a great extent by structural differences across the anode thickness. Potential measurements demonstrated the different dissolution behaviours across the anode thickness.

A simulation of the anode casting process was carried out and a basic model for anode solidification developed by using the experimental temperature data. The basic model showed realistic results and

can be used for the optimisation of the casting system, the cooling arrangement, and the mould design.

1 Introduction

Anode casting, which is the link between copper pyro- and hydrometallurgy, has a significant influence on both the chemical and physical anode quality, and hence determines anodic dissolution and electrorefining operations. Anodes must have a certain physical and chemical quality in order to provide uniform anodic dissolution and meet the requirements of electrorefining, namely to achieve a high current efficiency, low energy consumption, low anode scrap levels, and low personnel input together with high cathode quality. Various anode properties can be influenced directly by the casting process. Anode casting on casting wheels is the predominant casting technology, although it is associated with certain disadvantages regarding anode quality compared to CONTILANOD® anodes.

Previous studies, which were carried out by METTOP demonstrated that anode quality significantly affects electrorefining operations, especially at high current densities, which can be applied when using the new METTOP-BRX-Technology in the tankhouse. It was found that there are differences in dissolution between the air and mould side of the anode, and hence production of the corresponding cathodes, not only in the first cathodic crop, which would be consistent with the literature regarding variations in chemical quality in the outer anode areas, but also in the second cathodic crop, where the anode quality is considered to be homogeneous.

Investigations on casting wheel anodes were carried out to study the influence of the casting process on anode quality more in detail, and find optimisation potentials. An optimised casting process and corresponding higher anode quality would increase the current efficiency in the tankhouse and also allow the use of higher current densities, resulting in higher productivity.

2 Anode Quality Requirements

Anode quality depends on proper casting process control and has a significant influence on electrorefining.

The chemical quality criteria include a minimum content of harmful impurities, surface conditions of the anode body (especially the absence of passivating films), density, and the gas-saturation capacity [1, 2] and can be summarised as follows:

- For optimum electrorefining operations, the anodes should have a homogeneous chemical composition, so that the electrolysis can be adjusted properly for effective operation. Gas purging in the anode furnace is recommended for a uniform chemical composition within one charge.
- The elemental distribution within one anode is important for homogeneous dissolution.

- The accompanying elements in the anode should form soluble compounds with the copper or solid solutions, as insoluble compounds lead to high levels of Cu in the anode slimes or the formation of passivating layers on the anode surface.

The elemental distribution (and the grain size) can be adjusted by altering the solidification conditions, for example changing the cooling rate, thermal conductivity (i.e., material) of the anode moulds, and preheating the moulds. The level of non-metallic inclusions may be reduced by minimising slag carry-over from the anode furnace, metal-refractory interactions, as well as oxygen uptake during liquid metal pouring, for example using burners that provide a reducing atmosphere. The optimisation of mould wash (i.e., composition and amount) is also important as adhering mould wash can cause the formation of buds and dendrites. Preheating the anode moulds may be a suitable means to reduce the number of rejects.

Regarding physical quality, a uniform anode weight and therefore thickness, as well as smooth surfaces are essential for uniform anode spacing and hence dissolution. Variations in current density due to not perfectly vertical electrodes cause much more pronounced effects than other anode properties, for example the structure [3]. Anode preparation machines, which weigh, straighten, and mill the lugs, so that the anodes hang vertically in the cell and hence improve current distribution as well as enable higher current efficiencies at higher current densities, are becoming more prevalent [4]. Casting wheel anodes have a typical cast structure with inhomogeneous micro- and macrostructure over anode thickness due to the different cooling conditions from airside to mouldside. The anode requirements regarding physical quality can be summarised as follows:

- Independent of the technology used, proper control of the casting process is vital to produce high quality anodes with a uniform weight that are free from casting defects.
- As dissolution occurs preferentially at grain boundaries, anodes with a fine globulitic/equiaxed structure, and hence a lower (crystallisation) overvoltage, have a higher electrochemical dissolution rate at a given current density than those with coarse grains.
- Coarser globulitic/equiaxed grains are less susceptible to passivation.
- The grain size and the elemental distribution can be adjusted by altering the solidification conditions, for example a change of cooling rate, anode mould thermal conductivity (i.e., material), and mould preheating. Faster cooling results in finer grains and supersaturated solid solutions. The grain boundary structure is also linked to the elemental distribution, as the value of the distribution coefficient is determined by the cooling rate.

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 [5]. However, the literature statements concerning influence of grain size and DAS on passivation behaviour are not consistent [6-8].

The structure and elemental distribution can be influenced by solidification conditions, for example the cooling rate and heat transfer, and these in turn by:

- Mould material (thermal conductivity)
- Mould geometry

- Mould wash
- Amount of cooling water
- Mould preheating
- Thermal treatment of anodes
- Liquid anode copper casting temperature

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 [9, 10].

3 Experimental Investigations

As a first step, the actual casting conditions at Montanwerke Brixlegg AG, a secondary copper smelter in Austria, were determined. A temperature measurement system was installed in the anode moulds in order to determine the temperatures in the mould at defined positions (top/bottom/centre/side) and depths (140 mm/100 mm/50 mm/surface) and deduce the cooling conditions of the anodes. Furthermore, the temperature and the amount of the cooling water used for water spray cooling were measured. The corresponding anodes were analysed regarding physical and chemical quality, as well as dissolution behaviour. A casting parameter variation (i.e., mould material, mould wash, number of mould's days in use, mould geometry, amount of cooling water) was carried out in order to investigate their influences. The actual experiments, namely varying the cooling conditions, were accompanied by and compared with casting process simulations. A model for the simulation of anode casting was developed, which can be used to predict anode solidification and also the effects of mould design or cooling arrangement changes, which are currently determined by trial and error.

The experimental setup is described more in detail in [11].

4 Results

The casting process at Montanwerke Brixlegg AG is controlled very well, as visible from the narrow anode weight distribution (Figure 1).

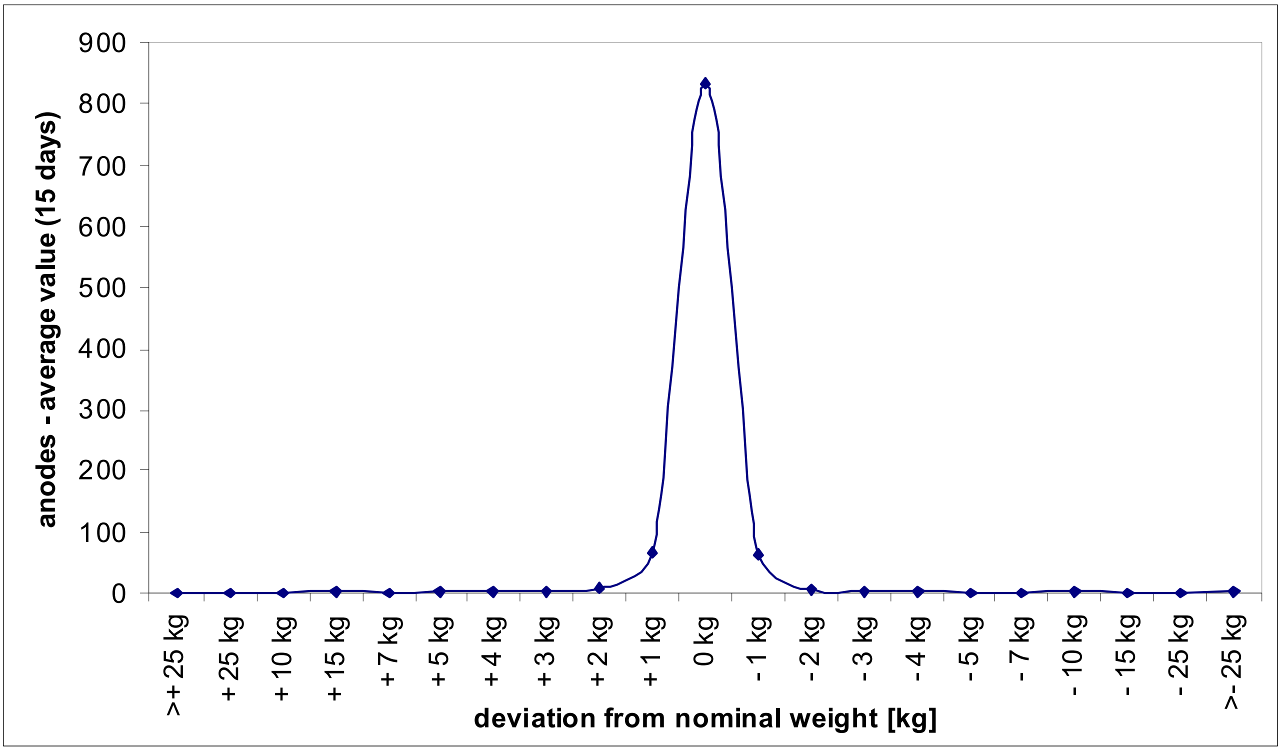

Figure 1: Average anode weight distribution (15 casting days)

Generally, during the casting process a relatively constant mould temperature was reached after several cycles, namely several anodes cast in one mould. A typical temperature curve is depicted in Figure 2. In this figure, the temperatures measured simultaneously at the measurement points in the centre of the anode mould are presented, as the most homogeneous conditions were found there due to the absence of influences from the edges. Each peak represents the casting of one anode. The wave-like form of the curve represents the mould filling and anode take-off. Interruptions in the casting process, for example due to mould casting or problems with anode take-off, are also visible from the temperature curves. The sample anodes for the investigations were always taken 3 hours after the start of casting, namely in the middle of the casting process, to avoid temperature instabilities due to mould casting and initial heating-up of the moulds. On some casting days an increase in casting temperature was measured towards the end of the casting process, which also led to an increase in mould temperature due to the higher liquid copper temperature. However, this increase did not occur on every casting day, and was a result of the specific furnace operations.

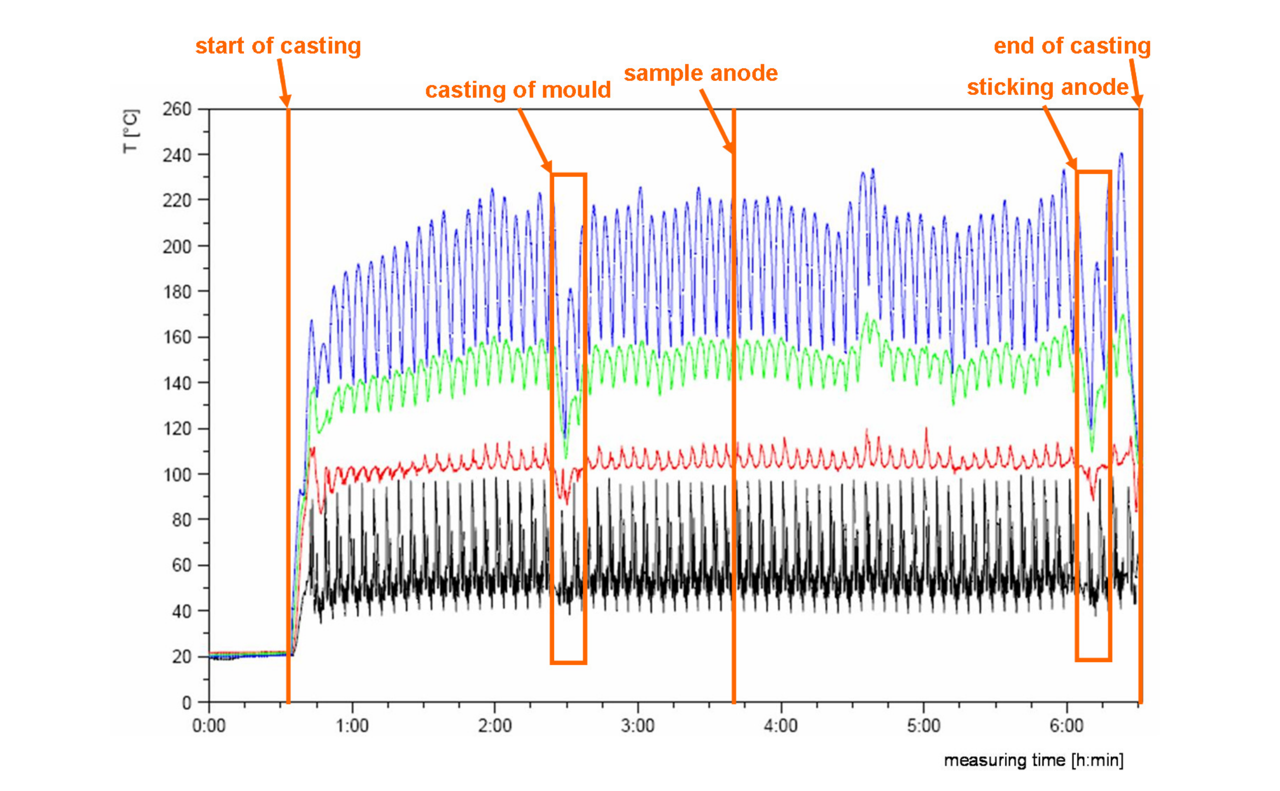

Figure 2: Typical temperature curve over the duration of the casting process-measurement points in the mould centre (blue: 140 mm, green: 100 mm, red: 50 mm, and black: surface)

The use of different mould materials and mould wash, as well as the different period of use of the mould, resulted in significant differences in mould temperature and hence anode cooling conditions (Figure 3 and 4). The rise in temperature with number of days in use (Figure 5) may have been caused by an insulating limescale, which formed on the mould bottom due to contact with the cooling water. To improve data comparison, the upper (i.e., maximum temperatures) and lower (i.e., minimum temperatures) envelope curves are depicted in the following figures, namely the range of temperature variations.

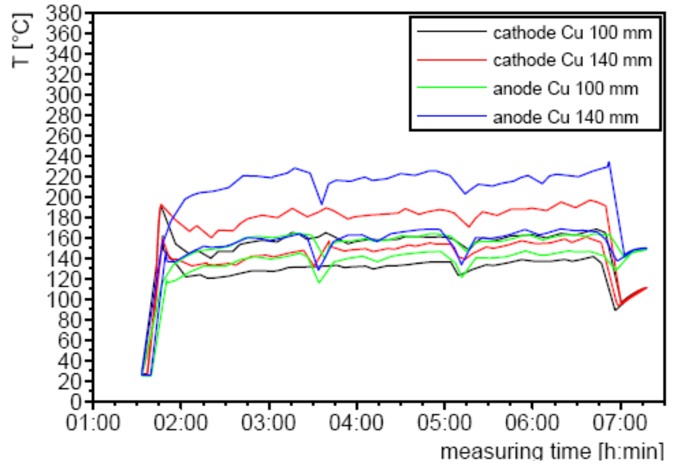

Figure 3: Temperatures in new anode and new cathode copper moulds on the same casting day (centre, 140 mm)

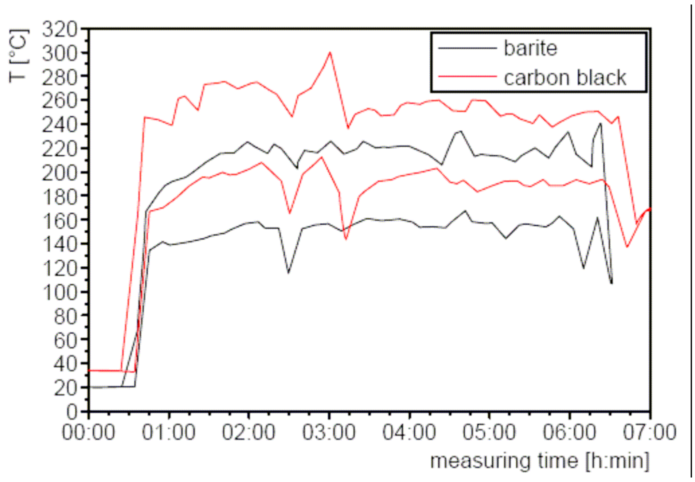

Figure 4: Effect of mould wash (centre, 140 mm)

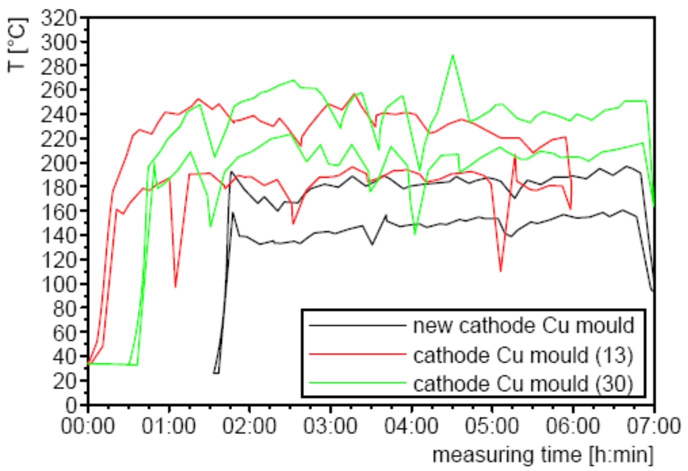

Figure 5: Influence of period of use of the mould (centre, 140 mm)

In general, the temperature differences between different depths were smaller in the moulds manufactured from cathode copper than in the anode copper moulds. This indicated a better, more homogeneous heating of the cathode copper mould, which may also be the reason for the delayed crack formation and finally the longer mould life compared to the anode copper mould. As the moulds were measured simultaneously, namely on the same casting day, an influence due to different casting temperatures on different days could be excluded. Higher temperatures and larger temperature variations between mould filling and take-off were visible for the anode copper mould compared to the cathode copper mould. The lower temperature of the latter can be explained by the higher thermal conductivity, which also led to a higher cooling effect. A higher cooling effect could also be achieved by a change in mould geometry, namely cooling ribs across the bottom of the mould. The use of carbon black resulted in higher mould temperatures compared to barite.

However, these temperature variations did not seem to have an influence on chemical anode quality, as - contrarily to literature statements - a relatively uniform chemical quality across the anode thickness, as well as the phase type and distribution, was found in all investigated anodes. No definitive trends regarding elemental distribution were detected. This may be due to the relatively rapid cooling at Montanwerke Brixlegg AG. Due to the use of gas purging in the anode furnace, the chemical composition within one batch of anodes, namely during the casting process, was found to be relatively constant.

Variations in structure were detected in the different anodes, namely across the anode thickness and over the anode area, which indicated different local cooling conditions. As there were no differences across the anode thickness due to chemical quality, the inhomogeneous anodic dissolution behaviour might be caused to a great extent by structural differences across the anode thickness. The anodes, which were produced with barite as mould wash, showed a typical cast structure (Figure 6). Variations in structure were detected in the different anodes. There was also a certain structural inhomogeneity within one anode, namely over the anode area, which indicated different local cooling conditions that may have been caused by uneven mould wash application as well as cracks in the mould. The variations in grain size directly on the air side, which solidifies in contact with ambient air, was probably caused by the different numbers of nuclei present. The variations in grain size close to the air side may have been caused by the Leidenfrost effect resulting in the formation of an insulating vapour film, which results in a lower heat transfer and hence reduced cooling efficiency. This could be avoided by applying atomised spray cooling or intermittent sprays, which avoid the formation of a stable vapour layer. The extension of the different solidification structures and hence the position of the central area was dependent on the cooling conditions at the air and mould side. The cooling was found to be very important, not only regarding anode quality but also regarding mould life and casting rate. A more effective cooling on the airside, namely the avoidance of the Leidenfrost effect, and a subsequent higher heat transfer on the air side would relieve the mould underside cooling and also reduce the thermal stress of the mould. This could prolong anode mould life. Additionally, at a constant mould underside cooling the casting rate could be increased. The insulating limescale on the mould underside could be avoided by using filtrated or recycled water. Even though the water temperature of the recycled water might be higher, the insulating limescale has a much more pronounced impact on the overall cooling effect.

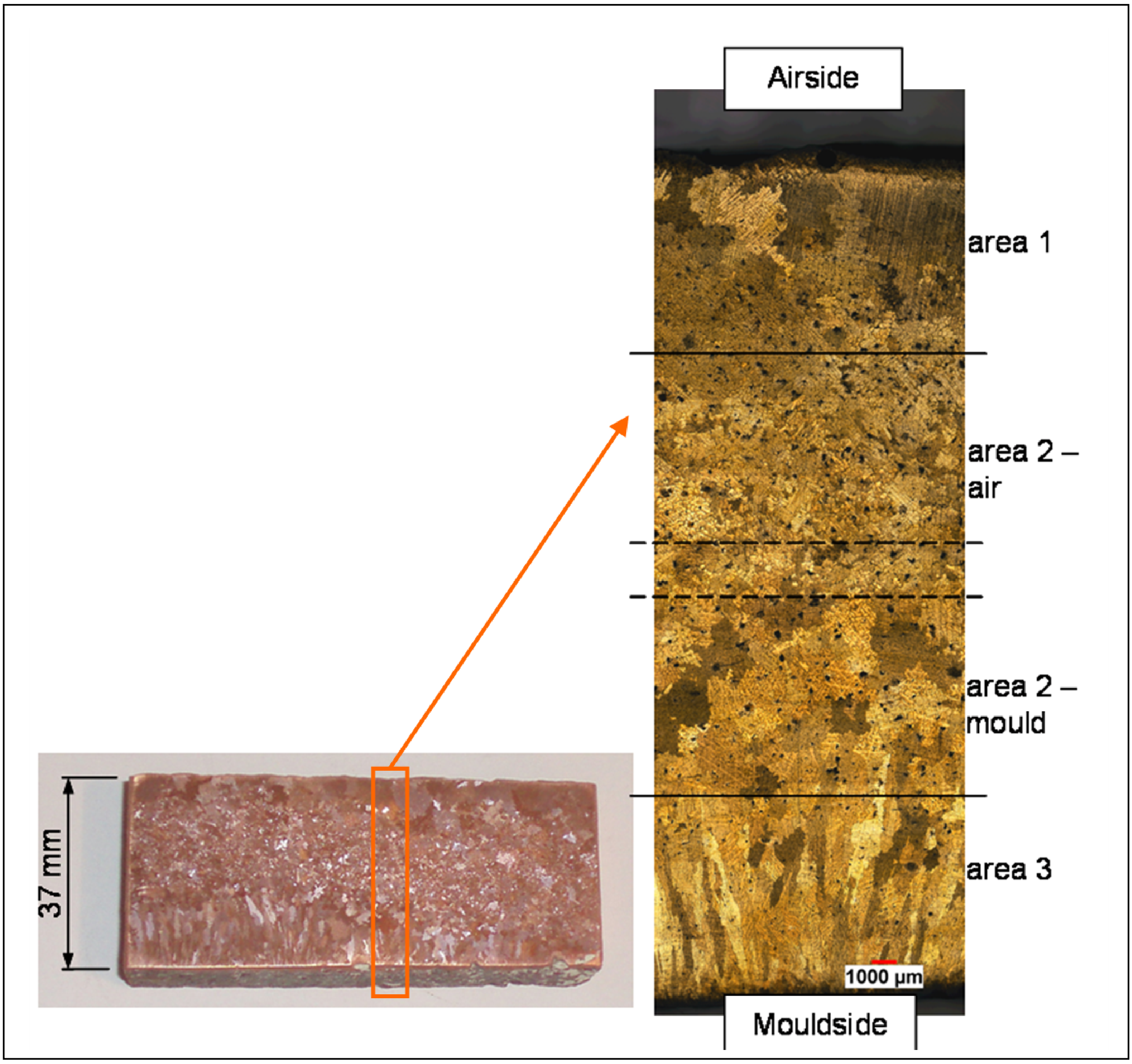

Figure 6: Macrostructure across the anode thickness

As dissolution occurs preferentially at the grain boundaries, the different solidification structures are reported to have different dissolution rates and tendency for passivation. Regarding electrochemical dissolution a less noble behaviour, namely fine grain, would be advantageous; regarding passivation a more noble behaviour and hence a higher anode polarisation for the onset of passivation would be desirable. The inhomogeneous anode dissolution in electrorefining could be explained by structure variations, namely grain size and secondary dendrite arm spacing (DAS), over the anode area and across the thickness. Potential measurements demonstrated the different dissolution behaviours across the anode thickness, namely the regions with different physical quality, namely differences in anode polarisation for onset of passivation and maximum current density i_{max}

(Figure 7). According to the experimental investigations, a homogeneous structure results in homogeneous anodic dissolution. However, no definitive correlation between the structure and the anode polarisation as well as the i_{max} could be found. Further investigations of a greater number of anodes with a wider range of structures would be necessary to find definitive trends for the anodic dissolution behaviour.

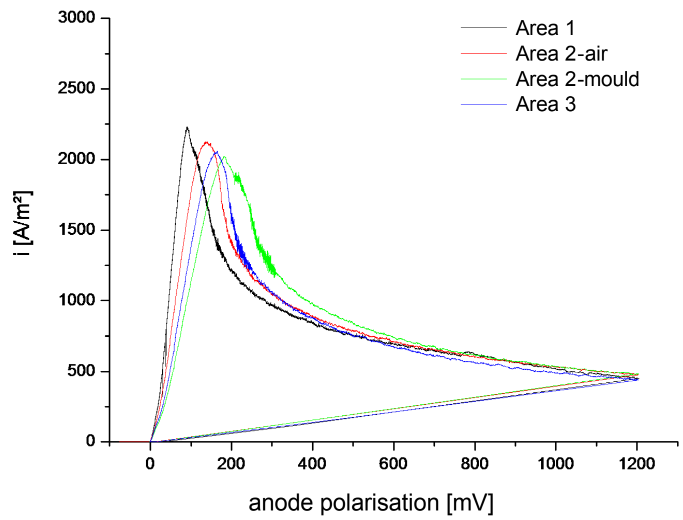

Figure 7: Anode polarisation scans

The variation of the process parameters (e.g., mould material, mould wash, and period of use of the mould) resulted in different mould temperatures and hence anode cooling conditions and anode quality. Besides these controlled parameters, some uncontrolled influences were determined that caused general quality variations between the anodes produced from one batch and within one anode:

- Casting temperature fluctuations
- Different mould wash densities
- Inhomogeneous mould wash application
- Different period of use of the mould/wear (e.g., cracks and limescale)
- Different mould material (i.e., anode copper batch from which the mould is cast)

Due to certain inhomogeneities in the overall process, the physical anode can vary significantly within one anode, as there are different local cooling conditions within one anode mould. Hence the cooling conditions of the anode can only be determined at those points where the temperature measurements are installed. Another parameter is the chemical composition of the anode copper, which has a certain variation range, as the nucleation of grains and also growth are linked to the impurities present. Due to the fluctuations in casting temperature, it would be reasonable to measure the casting temperature (and anode mould temperature) continuously and then adjust the cooling accordingly.

A basic model for the anode casting process was developed using the experimentally determined temperature data and a simulation of anode casting and solidification was carried out, which provides an overview of cooling and solidification. A simulation of grain size is limited by the present process variations. To perform this in a reasonable manner the following preconditions were required:

- Totally homogeneous moulds
- Totally homogenous mould wash and application
- Continuous measurement of casting and mould temperature, as well as continuous adjustment of cooling (only if the first 2 points are given, otherwise: cooling only suitable for positions with measurements but not for entire anode)

However, the calculated temperatures and solidification times together with the experimentally determined parameters to calculate DAS enable an estimation of the DAS in the anodes (Figure 8).

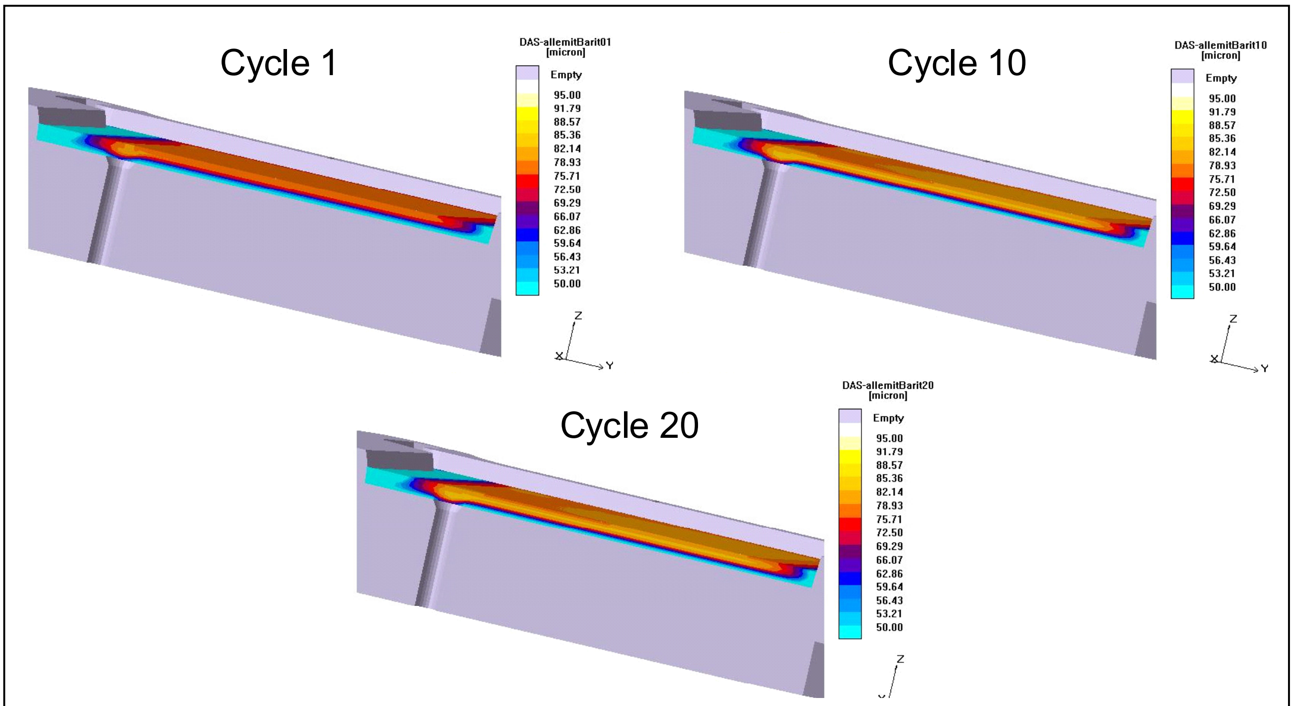

Figure 8: Calculated DAS

Calculations with different material data and cooling arrangements demonstrated the effects of cooling, mould geometry and mould material, and were confirmed by the experimental results. This demonstrated the general validity of the basic model for the simulation of anode casting. The basic model can be used for:

- Mould design optimisation
- Casting system optimisation
- Cooling arrangement optimisation

If a definitive relationship between DAS and anodic dissolution behaviour can be found by further investigations, also the prediction of the dissolution behaviour is possible by predicting DAS values. In order to not only predict the anodic dissolution behaviour from the cooling conditions, but predict the dissolution behaviour of each single batch, the model has to include also the chemical composition of the anode. A database of the dissolution behaviour of anodes with different chemical compositions has to be generated and linked with the model for the existing cooling conditions, so that finally the anodic dissolution behaviour of each single batch can be predicted by knowing the chemical composition.

5 Summary

The casting process on casting wheels and its influences on anode quality, as well as the influence of the latter on anodic dissolution and hence electrorefining operations were investigated. Anode quality has a significant influence on electrorefining operations, especially at high current densities, which are possible when using the new METTOP-BRX-Technology.

Within one anode, the physical quality variations seem to have a more pronounced effect on anodic dissolution than the chemical quality variations. Especially the physical anode quality can be adjusted by a variation of the casting process parameters (i.e., mould material, mould geometry, mould temperature, mould wash, and water spray cooling). Cathode copper moulds have a more homogeneous temperature distribution on the mould, a longer mould life, and better heat transfer due to better thermal conductivity, but also cause additional costs. Cooling is a very important parameter, not only regarding anode quality, but also regarding mould life. A more homogeneous anode structure results in more homogeneous anodic dissolution behaviour. A basic model for anode solidification developed by using the experimental temperature data and a simulation of the anode casting process was carried out. The basic model showed realistic results and can be used for the optimisation of the casting system, the cooling arrangement, and the mould design.

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