

THERMAL SHOCK OF ANODES – A SOLVED PROBLEM?

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ABSTRACT

An investigation is presented about the severity of the thermal shock to anodes set in the Hall-Héroult alumina reduction cell. The importance of the raw materials, the anode manufacturing process and the electrolysis cell conditions are demonstrated.

A fundamental formula is derived, which includes all relevant factors influencing the thermal shock behaviour of the anodes. Good qualitative agreement with practical experience is found.

INTRODUCTION

When a cold anode is set in the hot cryolite bath of the Hall-Héroult alumina reduction cell, a heat wave penetrates from the interface into the bulk of the anode. Depending on the local temperature distribution this causes thermal expansion of the material. Local differences in the thermal expansion of the anode leads to thermal stresses. Thermal shock can lead to anode cracking as shown in figure 1.

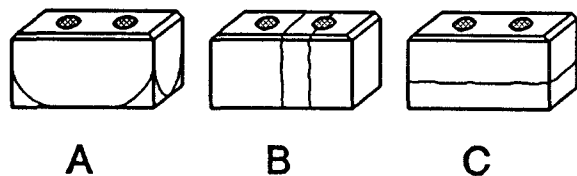


Figure 1: Three typical crack configurations due to thermal shock; A: corner cracks; B: vertical cracks; C: horizontal crack

Thermally cracked anodes lead to severe cell disturbance when pieces of carbon fall into the pot. A decreased aluminum production and a higher carbon net consumption are the highly expensive consequences.

STATE OF THE ART

First studies about the mechanical behaviour of a brittle solid placed under stress were carried out in 1913 by Inglis [1] and in 1920 by Griffith [2]. Griffith stated that strength is controlled by defects or flaws in the material ("Griffith flaw"). A crack can only propagate, if the elastic energy stored in the body is greater than the energy necessary to create a new fracture surface.

Based on the approach of Griffith, Hasselman extended the concept of thermal stress resistance calculation proposed by Kingery [3]. Hasselman defined a number of thermal shock (R) parameters to quantify the resistance to thermal shock of heterogeneous brittle solids by their physical properties [4, 5].

While the approach of Griffith is global, Irwin [6] calculated locally the stress intensity at the crack tip. He was able to link his theory with the Griffith approach, ie. the two concepts are compatible.

Modern theoretical indicators of the anode thermal shock resistance are primarily based on the above-mentioned approaches [7, 8, 9]. Empirically determined indicators have been published [10, 11] as well as results obtained from computer models [12, 13].

However the entire thermal shock problem of anodes is still not fully understood. Important characteristics of the inhomogeneous anodes, such as variability in mechanical properties or size and geometry effects in the electrolysis cell, have not been taken into account yet.

This paper gives an overview of all responsible factors affecting the thermal shock behaviour of the anodes. The causes of the influencing factors are separated into three groups:

- anode raw material quality
- anode manufacturing process
- electrolysis cell conditions

The relative importance of each factor regarding the thermal shock behaviour is investigated in this paper.

PHYSICAL DERIVATION OF THE THERMAL SHOCK RESISTANCE

When a solid body is heated up from the temperature T_0 to T_1 , it will expand according to

$$\epsilon_{th} = \alpha \cdot (T_1 - T_0) \quad (1)$$

where

ϵ_{th}	[-]	thermal expansion
α	[K ⁻¹]	coefficient of thermal expansion

If the thermal expansion can not take place due to exterior restraints of the body, elastic strain has to compensate the thermal expansion. Thermal stresses are thus created:

$$\sigma_{th} = E \cdot \epsilon_{th} = E \cdot \alpha \cdot (T_1 - T_0) \quad (2)$$

where

σ_{th}	[N/m ²]	thermal stress
E	[N/m ²]	static modulus of elasticity

The critical temperature difference ΔT_c , at which failure of the material has to be expected, can be described as

$$\Delta T_c = \frac{\sigma_c \cdot (1 - \nu)}{\alpha \cdot E} \quad (3)$$

where

σ_c	[N/m ²]	fracture strength
ν	[-]	poisson ratio

In the case of a thermal shock, where heat transfer conditions and geometry of the body play an important role, ΔT_c is also a function of the dimensionless Biot number B . The Biot number quantifies the heat transfer rate and is defined as:

$$B = \frac{V \cdot h}{S \cdot \lambda} = \frac{L \cdot h}{\lambda} \quad (4)$$

where

V	[m ³]	volume subjected to thermal shock
S	[m ²]	surface area through where the heat wave penetrates
L	[m]	characteristic length of the anode: $L = V / S$
h	[W/m ² K]	conductive heat transfer coefficient
λ	[W/mK]	thermal conductivity

In practice, very shortly after setting the anode into the cell, the liquid cryolite will freeze around the anode and build up an isolating cover. This will reduce the heat transfer rate and hence decrease the Biot number B .

For small Biot numbers ΔT_c and B are inversely proportional [14], therefore

$$\Delta T_c = \frac{\sigma_c \cdot (1 - \nu) \cdot \lambda}{\alpha \cdot E \cdot L \cdot h} \quad (5)$$

For simplifying reasons it is assumed that the material's behaviour under stress is linear elastic until unstable crack propagation starts.

The stress intensity factor K_I quantifies the tensional stress field perpendicular to the crack tip. When K_I reaches a critical level K_{Ic} , unstable crack propagation will start, leading to complete fracture of the part. K_{Ic} is known as the fracture toughness and describes the resistance against unstable crack propagation as follows:

$$K_{I0} = \sigma_c \cdot \sqrt{\pi \cdot a} \cdot Y \quad (6)$$

where

K_{Ic}	[N/m ^{3/2}]	fracture toughness
σ_c	[N/m ²]	fracture strength (tension)
a	[m]	characteristic crack dimension
Y	[-]	dimensionless function depending on the geometry and mode of loading

The experimental determination of the fracture toughness is difficult for porous materials such as carbon anodes. However, the fracture toughness can be determined indirectly by measuring the fracture energy G [6]:

$$K_{Ic}^2 = \frac{2 \cdot G \cdot E}{1 - \nu^2} \quad (7)$$

where
 G [J/m²] fracture energy

The fracture energy (also known as the energy release rate) is defined as the energy necessary to create a new unit of fracture surface. The method for measuring the fracture energy of anode material is described in [15].

At this point a characteristic peculiarity of the carbon anode has to be taken into account: due to the inhomogeneous structure of the material with its widespread flaw size distribution the mechanical properties of the anode are scattered asymmetrically around the mean value. In particular, the anode cracking behaviour is best described by a statistical treatment based on the weakest link concept such as the Weibull approach [16]. Especially for survival probabilities above 98 % (which is the important range for the practical application) the Weibull distribution has shown to be more accurate than the Gauss distribution.

The Weibull diagram (see figure 2) shows the probability of survival (double logarithmic scale) as a function of the applied fracture energy (single logarithmic scale). The Weibull modulus m reflects the degree of variability in fracture energy. In the Weibull diagram m signifies the slope of the material's characteristic curve. The less the fracture energy scatters, the higher is the Weibull modulus m and accordingly the higher is the probability of survival of the material.

After the fracture energy of a laboratory sample series is measured, the Weibull concept is of great use to predict the survival probabilities of full size anodes taking into account the volume effect. The volume effect can be demonstrated by applying the weakest link theory to a simple chain model: a chain subjected to a tensional load breaks at its weakest link. When the broken halves are retested, they are stronger than the original length, because the former weakest link is already eliminated.

Analogically, the fracture energy G_{Anode} of a full size anode (with a given volume V_{Anode}) is lower than the fracture energy G_{Sample} of a sample core taken from the anode (with a given volume V_{Sample}):

$$G_{Anode} = G_{Sample} \cdot \left(\frac{V_{Sample}}{V_{Anode}} \right)^{\frac{1}{m}} \quad (8)$$

where
 G_{Anode} [J/m²] characteristic fracture energy of the full size anode
 G_{Sample} [J/m²] characteristic fracture energy of the sample core
 V_{Anode} [m³] stressed volume of the full size anode
 V_{Sample} [m³] stressed volume of the sample core
 m [-] Weibull modulus

The Weibull diagram (see figure 2) shows the influence of the volume and the Weibull modulus on the survival probability as a function of the applied fracture energy. It is assumed that two sample series have the same fracture energy mean value of 300 J/m² (which corresponds to a survival probability of approx. 50 %). However the variability in fracture energy is different ($m = 3$ and $m = 13$ respectively, which represents the actual widest range found in the practice). The resulting fracture energies of the full size anodes at the 98 % survival level differ remarkably from each other: less than 10 J/m² (for $m = 3$) vs. 125 J/m² (for $m = 13$).

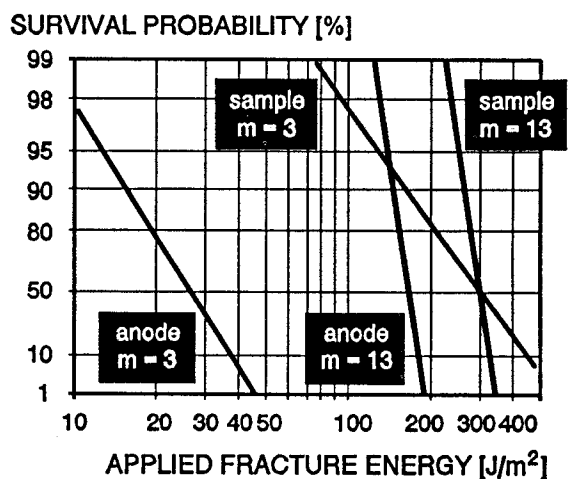


Figure 2: Weibull diagram showing the survival probability of two samples and anodes as a function of their volume, the Weibull modulus m and the applied fracture energy

Now equ. (6) - (8) can be fitted into (5). Equ. (9) represents the final thermal shock resistance (TSR), which can be interpreted as a dimensionless safety factor. The TSR is defined as the ratio between the critical temperature difference ΔT_c , at which failure of the material has to be expected, and the actual resulting temperature difference within the anode, after it is set into the cell:

$$TSR = \sqrt{\frac{2 \cdot G \cdot \left(\frac{V_{Sample}}{V_{Anode}}\right)^{\frac{1}{m}}}{\pi \cdot a \cdot E} \cdot \frac{2 \cdot \lambda \cdot (1 - \nu)}{\alpha \cdot L \cdot h \cdot Y \cdot \Delta T}} \tag{9}$$

where
 TSR [-] thermal shock resistance
 ΔT [K] difference between the bath temperature and the anode temperature before setting in the cell

The relevant temperature difference within the anode, which creates thermal stresses, is not directly measurable. However it is a function of the (easily measurable) temperature difference ΔT between the electrolyte bath and the anode, before it is set into the cell. Regarding the TSR, it is assumed that the relevant temperature difference creating the thermal stresses is equal to half of ΔT .

The practical significance of the TSR is the following:

- TSR > 1 No anode thermal shock failure is expected.
- TSR < 1 Anode thermal shock failure is expected.

PRACTICAL DETERMINATION OF THE THERMAL SHOCK RESISTANCE

The factors influencing the thermal shock resistance of the anode can be divided into three categories:

- raw materials
- anode manufacturing process
- electrolysis cell conditions

Table I shows the impact of these three categories on the parameters of the TSR.

In table II the TSR is first calculated for typical values found in the practice (first row). The resulting TSR = 1.53 signifies a safety clearance of 53 % towards the nominal value 1, where thermal shock damage would be expected. In order to compare the relative importance of each single factor, the TSR calculated for the typical values (ie. 1.53) is standardized to 100 %. The second and third row list the widest ranges of each factor towards the low and the high end respectively and the influence on the TSR. For proper interpretation of the results it has to be pointed out that the respective TSR is calculated with all other factors kept constant (ie. as typical values).

Table I The influence of the raw materials, anode manufacturing process and electrolysis cell conditions on the thermal shock resistance according to equ. (9)

factors	raw materials	anode manufacturing process:			electrolysis cell conditions
		mixing	forming	baking	
α	*				
E	*	*	*	*	
G	*	*	*	*	
m		*	*	*	
ν	*				
λ	*			*	
a	*	*	*	*	
Y			*		*
L			*		*
V_{Anode}			*		*
h					*
ΔT					*

Table II The relative importance of each parameter of the TSR as a function of the typical values and the widest ranges found in the practice

factors	unit	typical value	TSR typ. [-]; [%]	low end	TSR low [%]	high end	TSR high [%]
α	$10^{-6} K^{-1}$	4.00	} 1.53 = 100 %	5.00	80	3.00	133
E	$10^9 N/m^2$	4.50		5.50	90	3.50	113
G	J/m^2	190.00		160.00	91	225.00	108
m	-	8.00		3.00	32	13.00	130
ν	-	0.10		0.10	100	0.10	100
λ	W/mK	4.00		3.00	75	5.00	125
a	$10^{-6} m$	50.00		60.00	91	40.00	112
Y	-	8.00		9.00	89	7.00	114
L	m^3	0.13		0.19	70	0.08	169
V_{Anode}	m^3	0.30		0.72	95	0.06	229
h	W/m^2K	17.50	50.00	35	10.00	175	
ΔT	K	940.00	1050.00	90	760.00	124	

It is remarkable that a poor anode homogeneity (ie. low Weibull modulus m) leads to a similarly detrimental thermal shock behaviour as found for unfavourable electrolysis cell conditions (ie. high heat transfer rate h).

The variation of α of the cokes is due to the nature of the feedstocks and also due to the coking conditions.

A fuel coke showing a very fine mosaic texture of about 1 μm diameter with polarized light microscopy is defined as an isotropic coke having a high α value. A needle coke showing coarse flows and lamellar domains up to 100 μm length is defined as an anisotropic coke having a low α .

Influence of the Anode Raw Material

Typically a prebaked anode consists of up to 65 % petroleum coke, up to 20% recycled anode butts and up to 15 % coal tar pitch. In the following figures the large impact of the raw material quality on the anode thermal shock resistance is shown.

An alternative method to the so-called Optical Texture Index (OTI) [17] has been developed by Hume [18] to characterize the isotropy of the coke. The measurement of the pore axial ratio distribution using image analysis

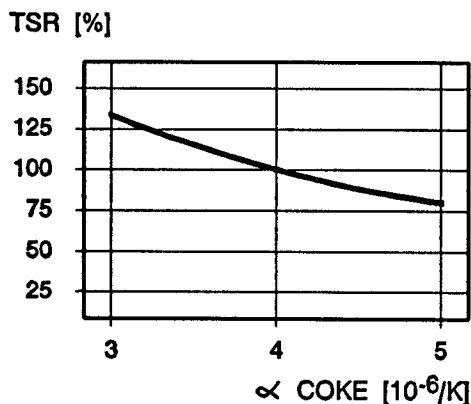


Figure 3: Influence of the coefficient of thermal expansion (α) of the filler coke on the thermal shock resistance (TSR) of the anode

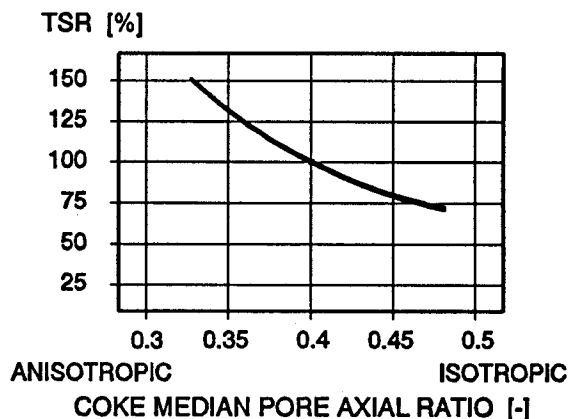


Figure 4: Influence of the median pore axial ratio of the coke on the thermal shock resistance (TSR) of the anode

allows the prediction of the coefficient of thermal expansion and thus the TSR as shown in figure 4, assuming all other factors are kept constant.

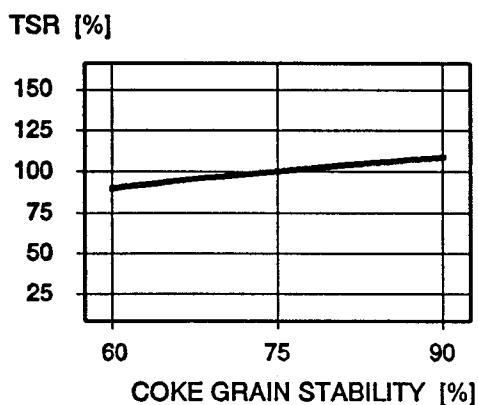


Figure 5: Influence of the grain stability of the coke on the thermal shock resistance (TSR) of the anode [20]

Another factors that influences the anode fracture energy and hence the TSR is the grain stability of the coke, as shown in figure 5 [19]. This property is sensitive to the presence of cracks and flaws in the coarse grains which can be controlled by appropriate calcination conditions of the coke.

Of course a very low porosity coke leads to dense anodes which may turn out to be brittle if the pitching is not reduced accordingly.

In the worst case, the combination of a low grain stability, low porosity, isotropic coke used in an unoptimized manufacturing process will lead to the most severe thermal shock problems [21].

Influence of the Anode Manufacturing Process

With a variation of the recipe (pitch / dust content and the dust fineness) the thermal shock relevant anode properties can be changed quite dramatically. Generally an optimisation has to take into account the following two considerations:

1. Theoretically a high anode quality is obtained by a recipe with high dust content and fine dust fineness which requires a great amount of pitch. In reality however this will lead to mixing difficulties (uneven pitch distribution) followed by baking problems (pitch devolatilisation leads to high gas pressure creating thermal cracks). Eventually, poorer anode quality is achieved.

2. In order to avoid mixing and baking problems, a recipe with low dust content and coarse dust fineness is favourable, thus the necessary amount of pitch is decreased. However, a lack of binder matrix will lead to a low overall burning quality of the anode.

Therefore the optimum recipe has to be chosen in accordance with the mixing and baking conditions.

The amount of recycled butts added to the green paste is largely determined by the anode consumption and is hence a rather invariable parameter in a given smelter, except during the start-up period [22]. However the method of butts addition (ie. separated or blended cokes and butts streamlines) has a great influence on the resulting anode quality. In the case of a blended streamline, fluctuations in the fines composition occur. The amount of pitch can not be adjusted properly, because the pitch requirements of butts and cokes are different. Local over- and underpitched anodes result with poor and widely scattering physical properties.

Figure 6 demonstrates the influence of the specific mixing energy of a Ko-kneader on the thermal shock resistance. A low mixing energy leads to a green paste with unevenly distributed pitch resulting in anodes with widely varying, low fracture energies.

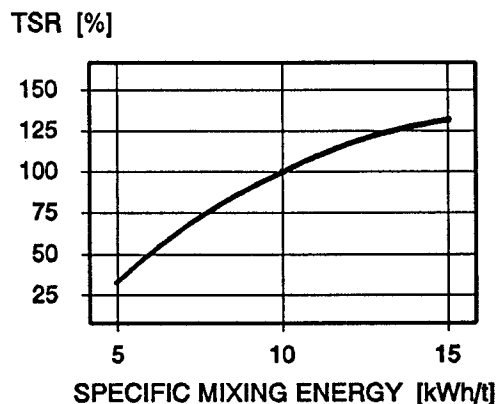


Figure 6: Influence of the specific mixing energy of a Ko-kneader on the thermal shock resistance (TSR) of the anode

Figure 7 shows the influence of the final baking temperature on the thermal shock resistance. The thermal conductivity increases exponentially with the final baking temperature due to the increasing alignment of the crystallites. The drawback of a higher baking temperature is the decreased baking capacity due to the longer baking time of the anodes. As well, too high a thermal conductivity can lead to airburn problems of the anodes in the electrolysis cell.

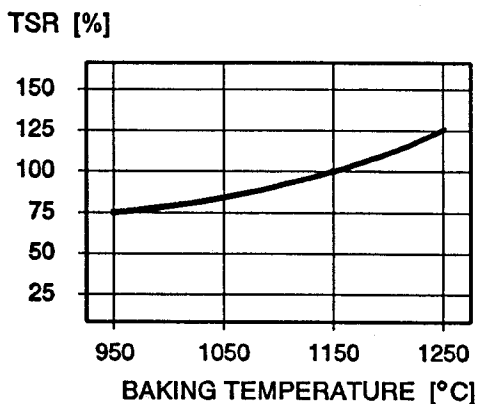


Figure 7: Influence of the final baking temperature on the thermal shock resistance (TSR) of the anode

In order to achieve a higher baking efficiency, the anode baking temperature gradient could be increased. However this leads to pitch devolatilization problems. Due to the higher gas pressure, cracks can be created lowering both the Weibull modulus and the fracture energy drastically (see figure 8).

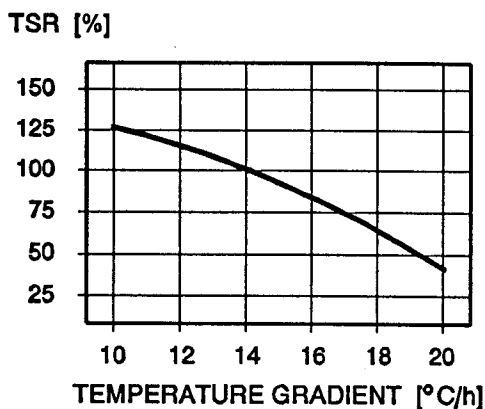


Figure 8: Influence of the anode baking temperature gradient between 200 and 600 °C on the thermal shock resistance (TSR) of the anode

Influence of the Electrolysis Cell Conditions

The conditions in the electrolysis cell have a strong influence on the thermal shock behaviour of the anodes. Even with anode properties on the safe side due to high quality raw materials and impeccable processing, thermal cracking can occur if cell conditions are unfavourable.

When the anode is set into the reduction cell, a heat wave starts to penetrate from the liquid electrolyte into the bulk of the anode. Due to the anode temperature being far below the freezing point of the cryolite, a thin layer of bath freezes around the anode forming a solid crust. This crust acts as a thermal insulator towards the anode. So the crust has the positive secondary effect of being a protective coating as far as anode thermal shock is concerned, even though while the crust around the anode remains frozen, no alumina can be reduced at the anode.

The predominant factor determining the severity of the thermal shock is the heat transfer rate into the anode. The amount of heat penetrating into the anode depends on factors such as:

- a) temperature difference ΔT between bath and anode
- b) metal and bath movement due to magnetic and convection effects
- c) immersion depth and size of the anode

Temperature Difference between Bath and Anode

A high bath temperature leads to a thinner cryolite crust around the anode. The effect of the thermal insulation is hence decreased, resulting in a higher heat exchange from the bath to the anode. Since the crust thickness is a function of location and time and since the heat transfer rate can not be measured directly, only a quantitative approximation of this effect can be given in figure 9.

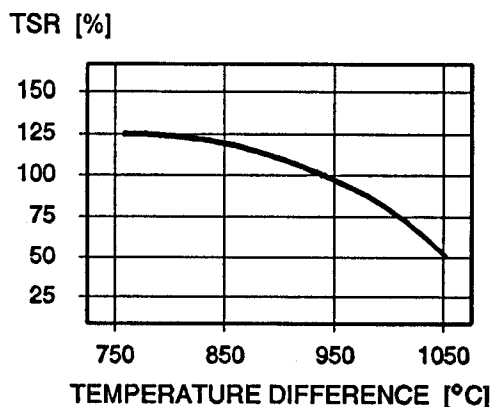


Figure 9: Influence of the temperature difference between the bath and the anode on the thermal shock resistance (TSR)

In practice the bath temperature can be controlled by the inter-polar distance, the metal level in the pot and the amount of alumina filled on the top of the frozen ledge. If the metal level is raised, more heat can penetrate through the side walls. The bath temperature is thus lowered. The same effect can be achieved by decreasing the layer of

the alumina on the top of the frozen ledge. The heat can flow straight upwards which decreases the bath temperature accordingly. Attention has to be paid though to the increased risk of airburn attack to the anodes.

Preheating the anode before it is set in the electrolysis cell is another possibility to decrease the temperature difference ΔT . Usually this is done by first positioning the anode at the height such that the bottom surface is just above the bath level. Of course, additional cost arise with this procedure due to the extra working step.

Metal and Bath Movements due to Magnetic and Convection Effects

Apart from the cell design the condition of the frozen ledge covering the sidewalls of the cell has a tremendous influence on the thermal shock severity of the anodes. It determines whether horizontal current components arise which cause metal movement due to magnetic effects. Common forms of metal movements are

- rotation
- upheaval
- oscillation (longitudinal, transversal or circular)

To a certain extent these metal movements are transferred to the electrolyte bath. A moving bath washes out the cryolite crust around the anode and intensifies the heat exchange to the anode.

A thermally well balanced electrolysis cell is shown in figure 10 a). The lower part of the side ledge is in line with the edge of the anode. Therefore the current flow through the metal is predominantly vertical. Metal and bath movement are thus minimum.

If the temperature of the metal is too low, the ledge extends underneath the anode. This can be caused by an elevated thermal conductivity of the bottom cathode blocks (\rightarrow cell design problem) or by the interpolar distance being too small (\rightarrow cell operation problem). Then the outer current flow is directed more towards the center of the cell, as shown in figure 10 b). The resulting horizontal current components cause metal movement accompanied with the above mentioned negative impact on the anode thermal shock resistance.

Conversely with the metal temperature being too high, the ledge is reduced which shifts the current flow through the metal towards the outside of the cell (figure 10 c). Consequently, unfavourable horizontal current components are created.

In addition to that, the anode bottom surface adjusts its shape to the metal level: In the case of an inclined anode

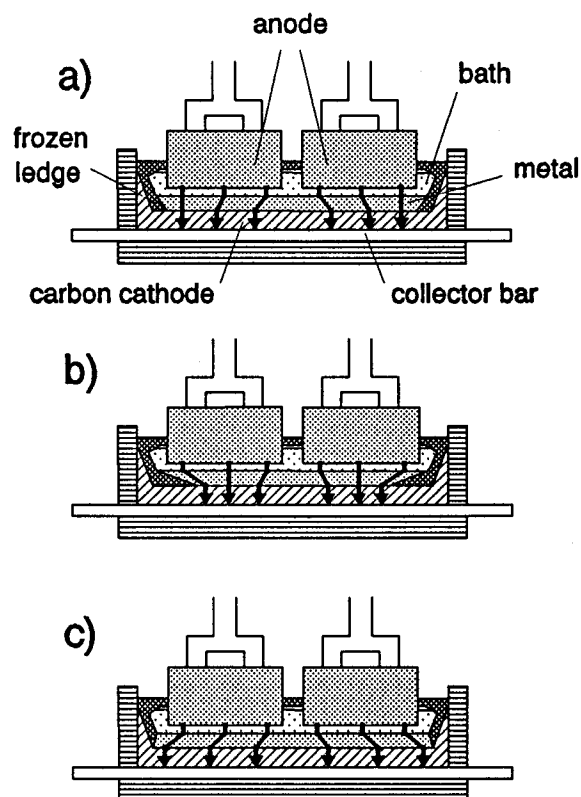


Figure 10: Influence of the frozen ledge profile on the direction of the current flow through the metal pad

bottom surface the reaction gas bubbles rise all on one side of the anode which leads to an increased heat exchange on that side due to the stronger convection.

In connection with the magnetic effects, the cell amperage has to be discussed as well. Modern electrolysis cells are designed to operate with steadily higher current intensities as well as bigger anode carbon blocks. Besides the general resulting effect of an increase in the magnetic fields due to a higher cell amperage (which leads to a greater metal and bath movement), the role of the anodic current distribution is becoming more important. Due to different ages and temperature distributions of the anodes the current through the anodes is never uniform. In a high amperage cell with an uneven current distribution the resulting metal movement can become highly critical. One way to avoid this problem is to set the new anodes as low as possible in order that they can pick up current more rapidly. However a greater immersion depth leads to an increased risk of thermal shock damage, as shown below.

Immersion Depth and Size of the Anode

As already mentioned above, the thermal shock severity in the electrolysis cell can be reduced by minimizing the heat exchange to the anode. In regards to geometrical aspects, this means that the anode surface area contacting the electrolyte should be minimized. The less the anode is immersed in the bath, the smaller is the amount of heat that can penetrate into the anode (due to the contact surface area) and the smaller is the volume affected by the thermal shock (ie. the chance of a low fracture energy area according to the Weibull statistics). The impact of the immersion depth on the thermal shock resistance is shown in figure 11 for different anode sizes. The dimensions of the different anode bottom surface areas used for the calculation are 800 x 530 mm (small anode), 1400 x 720 mm (medium anode) and 1430 x 1000 mm (big anode). It can be concluded that the size of the anode is of the same importance as the immersion depth.

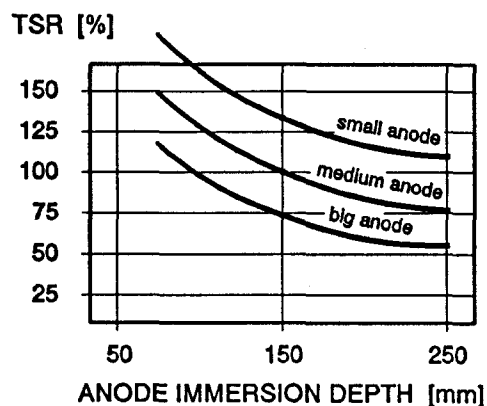


Figure 11: Influence of the immersion depth and the bottom surface area of the anode on the thermal shock resistance (TSR)

CONCLUSIONS

The factors affecting the thermal shock behaviour of carbon anodes are influenced by the quality of the anode raw materials, the anode manufacturing process and the electrolysis cell conditions. The relative importance of these factors on the overall thermal shock problem can be estimated as equivalent to each other. A dimensionless quality figure (TSR), indicating the thermal shock resistance, is derived and includes all thermal shock relevant factors.

An anisotropic, needle-like coke having a low coefficient of thermal expansion and a high grain stability is a most favourable raw material for a high thermal shock resistance of the final anode.

During the anode manufacturing process the main goal is to produce as homogeneous an anode as possible having the least variations in physical properties. A coarse recipe with a moderate amount of pitch content will reduce mixing and baking difficulties and thus increase the Weibull modulus and the fracture energy. An intensive mixing of the green paste (ideally combined with an efficient preheating and recooling unit) as well as a slow baking temperature gradient are both most favourable for the thermal shock resistance.

The conditions in the electrolysis cell should be kept in a way that the heat exchange from the electrolyte bath to the anode is as mild as possible. Ie. low superheat, little metal and bath movement, small immersion depth as well as small anode size are favourable.

Finally, due to the complexity of the anode thermal shock behaviour, a close collaboration between the anode manufacturer and the electrolysis cell operator is of utmost importance, when an arising thermal shock problem is to be solved efficiently.

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