AN APPROACH FOR A COMPLETE EVALUATION OF RESISTANCE TO THERMAL SHOCK

[1] Applying to the case of anodes and cathodes

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Abstract

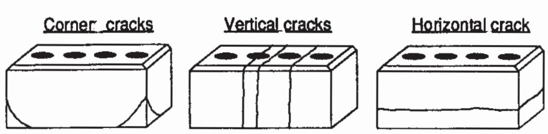
The aim of this paper is to describe a new method for characterizing a material in terms of resistance to thermal shock. Such characterization takes into account the criteria of thermal shock resistance to initiation (KINGERY criterion) and propagation (HASSELMAN criteria). It can be applied equally well to hard or soft thermal shock. This next approach has the following main advantages:

- Characterization of the material in terms of thermal shock is complete.
- Thermal shock tests or empirical formulae become unnecessary.

Examples of utilization of this new approach are presented for anodes and cathodes.

Introduction

When a cold anode is introduced into an electrolytic pot, it undergoes thermal shock as it comes into contact with the electrolytic bath which is at 950°C. Sometimes, this thermal shock can cause partial or total fracture of the anode.
The following sketch illustrates the three types of fracture that can happen in practice:



These three types of fracture are often mentioned in the literature [1], [2], [3], [4].
The cracking of a piece of the anode that falls into the pot will not only significantly perturb the operation of the pot, but will also deteriorate the working conditions for the operators and increase carbon consumption.
Hence, it is an essential criterion of quality that anodes be highly resistant to thermal shock.

State of the art

Modelization of thermal stresses makes it possible to explain and understand the three types of anode fractures listed

Modelization of thermal stresses enables calculation of the thermodynamic stresses and deformations induced in the anodes at the time of their introduction into the pot. Three studies have been published [5, 6 and 7]. The results explain perfectly the observations made on the shop floor.
Fracture deformation, which corresponds to the sensitivity of the material to tensile forces, may be higher than the deformation limit acceptable by the anode, thus leading to its fracture.

- Calculations confirm that, in certain cases, the stresses generated inside the anode exceed what can be withstood by the anode.
- In such cases, corner cracks occur within 5 to 25 minutes, and within the next half hour vertical cracks in the center of the anodes can also occur.
- Horizontal cracks can also be the result of thermal stress, although they only occur because of already existing cracks that are ready to expand in the anodes.

The anode fracture rate depends on the conditions of anode use

The influence of factors affecting the pots regarding the anode cracking rate has clearly been revealed on industrial pots [3] and confirmed by modelization calculations.
These factors are those that govern the quantity of heat penetrating the anode e.g.

- The temperature difference between the bath and the anode.
- The metal and bath movement.
- The depth at which the anode is immersed in the bath.
- The power dissipated inside the bath.

The anode fracture rate depends on the quality of the anodes

The quality of the anode, which can be assessed through its resistance to thermal shock, also affects the breakage rate. At the experimental level, two factors have been found to influence this quality: the **raw materials** on the one hand and the **process** on the other.

- Valco's industrial results [3] indicate the importance of these two factors: the nature of the coke, and the type of forming (pressing or vibrocompacting), as well as the adjustment of the pitch and fines contents.

- Laboratory results also mention the significance of these two factors: the resistance of anodes to thermal shock varies with the nature of the cokes [4 and 8], and increases with the mixing power [4] as well as with the final baking temperature [4 and 8].

The theoretical approaches of behavior to thermal shocks have led to the definition of several thermal shock resistance indicators

These approaches started in the field of ceramics [9 and 10]. A fairly recent summary report has been published following the application of these theories to carbon-loaded materials [11]. A few of these elements, indispensable for the comprehension of this paper, are described hereafter.

The notion of hard or soft thermal shock:

A **hard** thermal shock occurs when the speed at which the surface of a material (in this case the anode) becomes hot is much faster than the speed at which heat diffuses inside the same material. This corresponds to a situation where the material with a low thermal conductivity at a certain temperature is immersed into a bath which is at a significantly different temperature. In such a case, the surface of the material changes instantaneously and time is too short for the material to diffuse heat to its core. Consequently, the thermal conductivity of the material does not participate in the fracture mechanism. Similarly, thermal shock indicators will not take the thermal conductivity into account.
Conversely, the **soft** shock corresponds to a situation where the material has enough time to diffuse heat to its core. The higher the thermal conductivity, the better the diffusion of heat to the core. Temperature homogenization reduces the thermal gradients and thus minimizes the stresses to which the material is exposed. In such a case, the thermal shock resistance indicators take the thermal conductivity into account.
It should be noted that between these two extreme cases there are numerous intermediate cases in which conductivity plays only a limited role. This is the case for anodes.

The notion of initiation and propagation ofcracks:

KINGERY's thermoelastic approach [9] assumes a homogeneous, isotropic material with a perfectly brittle elastic linear mechanical behaviour. Kingery does not take the detail of solid material defects into account, but rather the defect initiation condition that causes the fracture. Thus he expresses the first two criteria of crack initiation resistance as:

Hard thermal shock $R_k = \sigma_R \bullet f(\nu) / E \bullet \alpha$ (°C)

Where: k refers to Kingery; E, σ_R, ν and α are respectively Young's modulus, the breaking stress, Poisson ratio and the coefficient of thermal expansion of the material. Rk corresponds to the maximum difference in temperature that can be withstood by the material without breaking.

Soft thermal shock $R'_k = k \bullet \sigma_R \bullet f(\nu) / E \bullet \alpha$ (W/m)

Where: k is the thermal conductivity of the material.
R'k corresponds to the maximum flux of heat per unit of length that can be withstood by the material without breaking.
HASSELMAN's energy-based approach [10] assumes that the material is already cracked and it studies the stability of the cracks with regard to thermally-induced stresses. It defines three criteria of resistance to crack propagation.

Short cracks $R'''' = \gamma_s \bullet E / \sigma_R^2$ (m)

where: γ_s is the energy required to increase the surface of the crack by one unit; R'''' corresponds to the dimension of the defect or of the crack.

Long cracks and hard shock $R_{st} = \sqrt{\gamma_s / E \bullet \alpha^2}$ (°C$\sqrt{m}$)

Long cracks and soft shock $R'_{st} = k \bullet \sqrt{\gamma_s / E \bullet \alpha^2}$ (°C$\sqrt{m}$)

The higher the above criteria, the higher the resistance to thermal shock of a material.

Impacts of these 2 approaches:

It is possible to mention at least two impacts which play a significant role:
- In order to determine the criteria of the resistance to propagation of cracks caused by thermal shock, it is necessary to determine the fracture energy which is a parameter difficult to measure. Such a measurement has thus been developed for carbon materials and has recently been mentioned in publications [11, 12, 13 and 17]. Hence, the measurement of resistance criteria to the propagation of cracks has been introduced only recently.
- The determination of the thermal shock resistance criteria makes it possible to classify materials according to their theoretical resistance to thermal shocks but since the decisive criteria involved in the anode fracture mechanism is not known, a new debate has emerged: is the anode fracture mechanism governed by the initiation or the propagation of the crack, or in other words, is the resistance to initiation higher than the resistance to propagation ? Since there is no answer to this question, there has not been, contrary to expectations, any change of attitude to the problem of thermal shock to anodes. The following two attitudes have remained:

The first has been to continue developing thermal shock tests [15, 16, and 2] with the unreadily solved problem of how to make the test representative of industrial reality, which is difficult to demonstrate.
The second has been to define an empirical global criterion accessible by the determination of physical characteristics of the material [1, 7, 4], the validity of which must also be demonstrated.
The purpose of the present paper is to present a new approach which is a method for evaluating resistance to thermal shocks based on the use of a diagram that takes into account the theoretical criteria of initiation and propagation of cracks developed by Kingery and Hasselman.

Principle of the new approach

The adopted approach can be described in two steps:

Experimental determination of thermal shock resistance criteria

This necessitates good knowledge of the following characteristics:

The case of hard shock:

- Flexural strength (F) which corresponds to the breaking stress. It represents the conditions of thermal shock in as much as the cracking is caused by a tensile strength.
- Young's modulus (E).
- Coefficient of thermal expansion (α).
- Fracture energy (γ_s).

The Poisson ratio is assumed to be constant. This approximation is currently accepted.

The case of soft shock:

An additional characteristic, thermal conductivity, must be measured.

Given these elements, the thermal shock criteria are reduced to the expressions given in the following table:

	HARD	SOFT
• Crack initiation	$R_k = F/E \cdot \alpha$	$R'_k = k \cdot F/E \cdot \alpha$
• Crack propagation		
Short cracks	$R'''' = E \cdot \gamma_s/F^2$	$R'''' = E \cdot \gamma_s/F^2$
Long cracks	$R_{st} = (1/\alpha) \cdot \sqrt{\gamma_s / E}$	$R'_{st} = (k/\alpha) \cdot \sqrt{\gamma_s / E}$

Drawing up thermal shock resistance diagrams

These diagrams are based on mathematical relationships which link the three thermal shock criteria in each of the two extreme cases:

Hard shock $\boxed{R_{st} = R_k \cdot \sqrt{R''''}}$

Soft shock $\boxed{R'_{st} = R'_k \cdot \sqrt{R''''}}$

The graphic representation of these two relationships gives the two diagrams shown on figures 1 and 2.

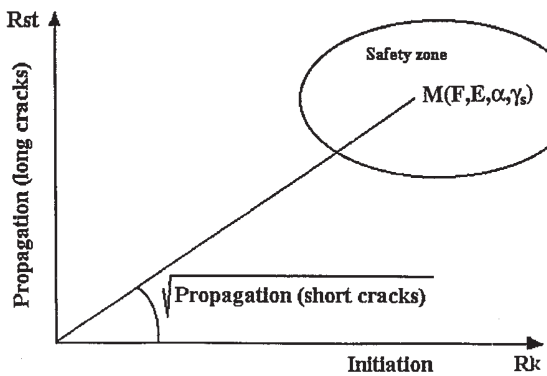


Figure 1
Diagram for HARD thermal shock.

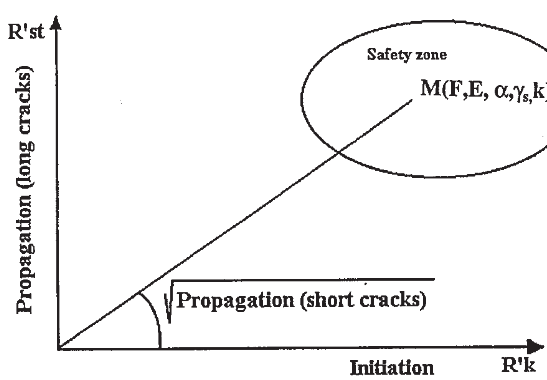


Figure 2
Diagram for SOFT thermal shock.

The ordinate of each diagram corresponds to the long crack propagation resistance criterion: R_{st} or R'_{st}.
The absciss of each diagram corresponds to the crack initiation resistance criterion: R_k or R'_k.
The slope of the straight line that links up the origin to point M, has a value which is the square root of the short crack propagation resistance criterion: $\sqrt{R''''}$.

Determining E, F, γ_s, and α makes it possible to position the carbon material on the diagram. Thus the material will be characterized by the three indicators Rst, Rk, R"" and R'st, R'k, R"" for hard shocks and soft shocks respectively.
Materials with a high resistance to thermal shocks (initiation and propagation), will be located in the top right hand part of the diagram, as the three resistance criteria are high in this zone.
It can be seen immediately from this diagram that there is no systematic conflict between the resistance to crack initiation and the resistance to crack propagation.
Hence, the thermal shock resistance of the carbon material can be characterized by its position on these diagrams.

Experimental procedure

- Flexural strength (F) is the result of a 3-point bending measurement carried out on cylindrical test specimens (dia. 50 mm, length 150 mm), using an INSTRON type 1343 500KN press.
- The Young's modulus (E) measured is a dynamic one. It is measured on the same test specimens as above using a GRINDO SONIC type MK4 apparatus manufactured by Lemmens Co.
- The coefficient of expansion (α) corresponding to a mean coefficient of expansion ranging from 50 to 500°C is measured on cylindrical test specimens (dia. 12 mm, length 50 mm) using dilatometers ADAMEL LHOMARGY type DI 24 controlled by a Logidil software.
- Thermal conductivity (k) is measured on disk test specimens (dia. 50 mm, height 20 mm), using a R & D CARBON type 143 apparatus.
- The fracture energy (γs) is determined from a 3-point bending test cycle on a parallepipedic test specimen, one face of which includes a notch intended to localize the crack that extends during the test. The detailed procedure is described in the reference article [12]. Note that there were two sizes of test specimens in order to enable testing not only the industrial test specimens but also test samples from benchscale anodes:
  W = 40 mm B = 30 mm Length = 170 mm
  or W = 50 mm B = 40 mm Length = 400 mm
  The tests made it possible to confirm that the results obtained did not differ as a function of the size of the test specimens.

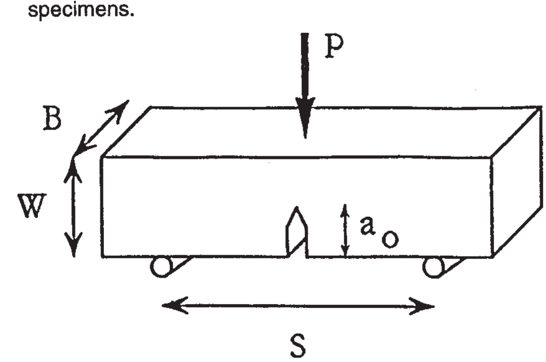


Figure 3
Three-point bending test on single. Edge notched beam.

Remark: Since anodes and cathodes are not isotropic, the direction in which the characteristics are measured must be precisely defined. The characteristics have always been measured in a direction perpendicular to the grain which corresponds to the weakest mechanical characteristics.

Results and discussion

The utilization of thermal shock diagrams is, in many cases, highly interesting. We will use only three examples to demonstrate the power of this tool for determining the resistance of carbon materials to thermal shocks.

- Parametric study on benchscale anodes enabling the importance of each parameter tested to be evaluated.
- Comparison of the thermal shock resistances of benchscale anodes and industrial anodes.
- Studies of other carbon materials.

To simplify the discussion, we chose to examine only the case of hard thermal shock for three reasons:

- In the case of a hard shock, the thermal shock diagram is more precise since the conductivity does not come into consideration and therefore does not bring additional uncertainty by its very own nature.
- Moreover, modelization studies published [6] and non published [8] have demonstrated that the impact of thermal conductivity was low since it had an exponent of 0.2 to 0.4 in the fracture mechanism. Thus the thermal shock experienced by the anodes was rather hard than soft.
- In most cases, the introduction of thermal conductivity in thermal shock criteria does not modify the relative positioning of the different points on the diagram.

Parametric studies on benchscale anodes

Overall results:

Overall results of the parametric study are shown in Figure 4 below:

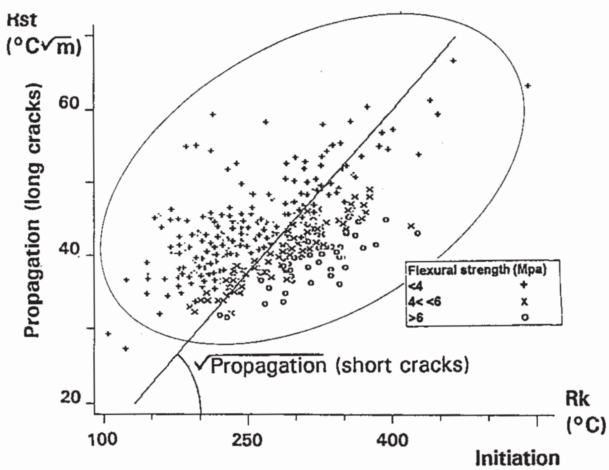


Figure 4
Resistance to thermal shock: results of the parametric study carried out on benchscale anodes.

Each point corresponds to an individual value and not to the mean calculation of several values.
All the points are within an ellipse the long axis of which is offset with respect to the straight line that links the origin to the barycenter of the cluster of dots.
Thus, it is easy to see that, globally, the more resistance to initiation increases (as shown by the absciss value), greater is the increase in resistance to the propagation of long cracks (as shown by the ordinate value). With regards to resistance to the propagation of short cracks (shown by the square of the slope of the straight line that links up the origin to the point considered), it tends to decrease slightly since, as stated above, the long axis of the ellipse does not cross the origin.

Therefore, if observations are limited to the zone explored, one can see that it is possible to maximize resistance to initiation and propagation of long cracks simultaneously while preserving a satisfactory resistance to short crack propagation.
Even if measurements of resistance to thermal shock are lacking in accuracy as they involve characteristics with rather numerous measurement errors, the diagram shows that the points which correspond to the strongest bendings have an overall lower resistance to the propagation of long and short cracks. The variations recorded on this diagram are statistically very significant as they are much more numerous than the measurement errors.

Example:

By way of example, figure 5 shown below represents the points corresponding to the study of the influence of the baked scraps content (between 0% and 66%) at a constant granulometric formulation and binder ratio.

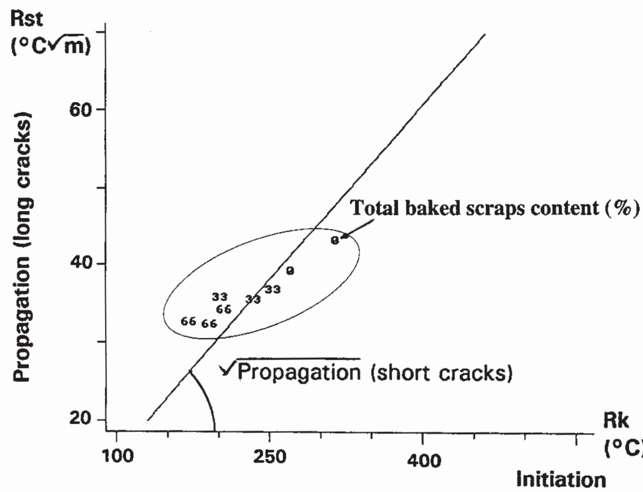


Figure 5
Influence of the baked scraps content on the resistance to thermal shock [benchscale anodes].

Several remarks can be made:

- In comparison to the ellipse already shown, the variations recorded during this study are fairly modest.
- If the content of recycled products is increased, the resistances to initiation and propagation of long cracks are reduced and the resistance to the propagation of short cracks is not or barely affected. This result is in agreement with the industrial observations: the sensitivity of anodes to thermal shock increases with the content of baked scraps.

Analysis of the results of the parametric study on benchscale anodes. Classification by size of the significance of each parameter:

The importance of a parameter can be assessed on the basis of the size of the ellipse (or more precisely the length of its projection on the diagonal axis of the diagram), which includes the points when this parameter is modified, and by comparing it with the long axis of the ellipse that contains all the points of the parametric study. Thus the relative significance of the parameters can be compared.
A full study has been carried out in which 10 parameters have been tested, and their relative importance evaluated

- The parameters tested and their fluctuation range.
  - Type of coke: since there were no specific constraints at the laboratory level, some of the cokes tested were significantly out of the industrial coke specifications.
  - Pitch content: the domain tested covered between 13% and 20%.
  - Type of pitch: as for the cokes, some of the pitches tested were significantly out of the industrial pitch specifications.
  - Mixing-compacting conditions: the mixing temperature varied between 150°C and 170°C and the forming pressure between 250 bars and 450 bars.
  - Coke calcination level: evaluated using the Lc, the level varied between 26A and 44A.
  - Recycled product content: it ranged between 0% and 66%.
  - Positioning of the recycled products: with a constant content of recycled products (25%), these have been introduced either in the coarse, medium or fine parts of the dry formulation.
  - Maximum size of the coke or recycled product grains ranged between 1.5 mm and 22 mm.
  - Baking temperature varied between 1100°C and 1300°C.
  - G/S ratio: this ranged between 2 and 14.

    The G/S is a gravimetric ratio of two granulometric fractions, G and S, which partly characterizes the dry formulation of the anode.

    This G/S ratio is a parameter specific to Aluminium Pechiney's carbon process.

    G (or Grain) represents grains > 300µm.

    S (or Sand) represents grains between 30µm and 300 µm.

    UF (or ultrafines) represents the remainder and is composed of grains < 30 µm.
- Results

  The order of importance of the influence of the 10 parameters tested on the resistance to the thermal shock of an anode is shown on figure 6.

  There are two strongly influencing factors:
  - The type of coke.
  - The dry formulation characterized on the diagram by the G/S ratio.

  There are factors that have a modest influence:
  - The baked scraps.
  - The baking final temperature.

  There are factors that have a negligible influence:
  - The type of pitch.
  - The mixing-compacting conditions.
  - The coke calcination level.
  - The positioning of the recycled products in the coarse or fine grains.
  - The maximum grain size.
  - The pitch content.

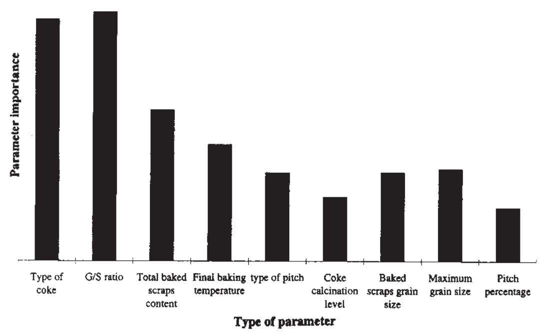


Figure 6
Influence of the different parameters tested on the resistance to thermal shock (benchscale anodes).

<u>Utilization of the thermal shock resistance diagram on industrial anodes. Comparison with benchscale anodes</u>

On the thermal shock diagram shown in figure 7, the industrial anodes from several smelters are within an ellipse, the barycenter of which has practically the same absciss as that of the benchscale anodes. Conversely, the ordinate of this barycenter is notably lower. The flexural strength results that appear on the diagram below are much higher than that for the benchscale anodes but are well in line with the results of the benchscale anodes.

Thus, overall, industrial anodes offer a resistance to crack initiation similar to that of benchscale anodes. Conversely, resistances to the propagation of short and long cracks are weaker.

This difference between benchscale and industrial anodes leads us to hope that the resistance to propagation of industrial anodes, hence the overall resistance of these anodes, could be increased without affecting the other characteristics.

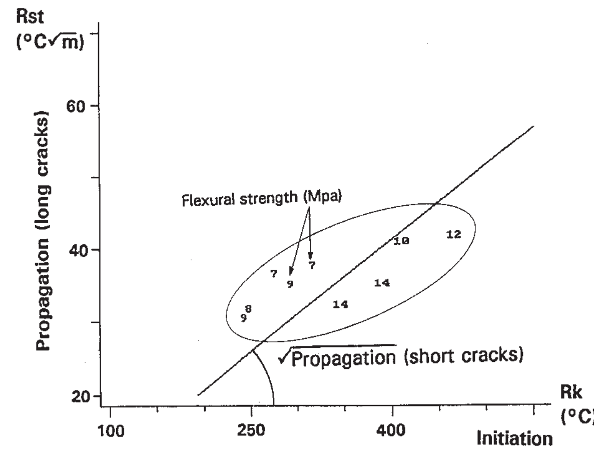


Figure 7
Thermal shock resistance diagram: application on industrial anodes. Weight of the flexural strength.

<u>Application to the cathodes</u>

The comparison is done on industrial samples.

- The diagram in figure 8 shows that the ellipse that embodies all the cathodes (purely anthracitic cathodes (A), semi-graphite cathodes (B, C and D with respectively 20%, 30% and 50% graphite), graphite cathodes (E), graphitized cathode (F), is much larger than that of the industrial anodes, due probably to the large range of raw materials used (from anthracite to graphite).
- The cathode diagram clearly shows a hierarchy in the resistance to thermal shock which "matches" reality. Indeed, the points corresponding to the graphite cathodes (E) and to graphitized cathodes (F) are those which correspond to the best resistances to initiation and propagation of long cracks; it is well known that these two types of cathodes are those which accept most easily the cathode bar cast iron sealing stage during which they withstand a significant thermal shock.
- Besides, the fact that industrial graphite and graphitized cathodes are more resistant to thermal shocks leads us to think that the overall resistance to the thermal shock depends more on the resistance to initiation and resistance to propagation of long cracks than on the resistance to propagation of short cracks.
- The anodes are at a rather weak level of resistance to propagation of long cracks thus confirming the idea that it can be improved.

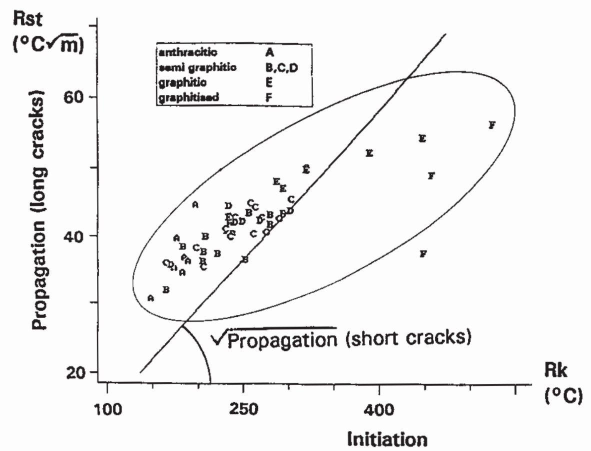


Figure 8
Thermal shock resistance diagram. Application to industrial cathodic material.

Conclusion

This paper describes a new approach for evaluating the resistance of a material to thermal shock by using diagrams, the main advantages of which can be summarized as follows:

- This approach can be rigorously applied to all types of materials for which the Poisson ratio can be considered as constant since it is the only approximation made to obtain simple mathematical relationships between the resistance to propagation of long cracks, resistance to initiation, resistance to propagation of short cracks, and the resulting diagrams.
- It fully characterizes the resistance of the material to thermal shock since it takes into consideration not only the resistance to initiation of cracks but also the resistances to propagation (long and short cracks).
- It can be applied equally well to hard and soft thermal shocks.
- It is validated by industrial results obtained on anodes and cathodes.
- It is more powerful and supercedes those studies aimed at defining thermal shock indicators specific to each of the materials and to each type of thermal shock.
- It renders the thermal shock test development methods useless, since they are often difficult to implement and their validity is always dubious.

In the second part of this presentation, we will describe a new approach for the practical resolution of a thermal shock problem in the ALBA plant in BAHREIN [19].

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