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EFFECTS OF COKE AND FORMULATION VARIABLES ON CRACKING OF BENCH SCALE PREBAKED ANODE SPECIMENS

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Bench scale anodes were prepared using a number of calcined cokes, aggregate sizings, and pitch levels and, after baking, tested for thermal shock resistance and flexural strength. Thermal shock resistance rose with increasing coke real density, while flexural strength tended to improve with increasing coke bulk density. With coarser aggregate sizings, a pitch level resulting in maximum baked apparent density maximized thermal shock resistance and flexural strength. With a finer aggregate sizing, thermal shock resistance and flexural strength peaked at a pitch level greater than that producing the highest baked apparent density, so maximum values require more pitch than probably practical for full-size anodes.

Introduction

With many Hall cell designs and under ideal operating conditions, prebaked anodes are not prone to cracking. Only factors such as excess carbon consumption and electrical resistivity need to be considered in selecting raw materials and formulation. However, at some smelters anode cracking is a problem of considerable magnitude. The devastating effect of large quantities of cracked anodes can overshadow and contribute to high excess consumption and electrical resistance.

Several types of anode cracking can occur due to thermal and mechanical stresses. Thermally induced cracks can result in spalling of corners from anodes shortly after being put into service. Vertical cracks emanating from the stub hole within a few days after the anode is put into service are caused by mechanical or thermomechanical-induced stresses. This is caused by pressure exerted by the expanding stub and possibly augmented by differential thermal expansion between the hotter anode bottom and cooler top. A similar crack sometimes occurs during rodding.

Although cracking problems can at times be alleviated by engineering changes, such as redesign of stub holes, or changes in anode setting procedures, such modifications are not always economically or technically feasible. Improvement of the intrinsic resistance of the anode carbon to cracking is often the most promising avenue. The paper (1) presented by Brown and Rhedey at the 1975 meeting discussed this subject in some detail but dealt with only a limited number of cokes and a single aggregate sizing. An earlier (1965) paper (2) by Harvey and Van Dyne was limited to one coke.

General

Work was carried out on a variety of calcined delayed cokes including petroleum cokes having a wide range in bulk densities, gilsonite coke, and coal tar pitch cokes. Some coke properties are given in Table I. Since coal tar pitch remains the dominant binder used in prebaked anode manufacture, binder was limited to coal tar pitch (110°C softening point, 12% quinoline insoluble).

Table I. Some Properties of Calcined Cokes Used for Anode Cracking Studies

Arbitrary Coke Designation	Type of Coke	Maximum Bulk Density, g cm^{-3}	Ash Content*, wt. %	Sulfur Content, wt. %	Real Density**, g cm^{-3}	Crystallite Height, nm
A	Gilsonite	1.342	0.86	0.30	1.96	2.7
B	Petroleum	1.333	0.51	0.84	2.03	3.2
C	Gils.-Pet.	1.319	0.79	0.30	1.97	2.8
D	Coal Tar Pitch	1.306	0.13	0.12	2.02	2.6
E	Coal Tar Pitch	1.300	0.14	0.12	2.07	3.3
F	Petroleum	1.286	0.25	1.18	2.05	3.2
G	Petroleum	1.247	0.30	1.00	2.07	3.5
H	Petroleum	1.226	0.20	1.74	2.06	3.3
I	Petroleum	1.194	0.28	1.01	2.04	3.2
J	Petroleum	1.150	0.22	2.33	2.06	3.4

*Determined at 750°C.
**Density of -200 mesh fraction in kerosene.

Aggregate sizings and binder levels used in each set of experiments are described below.

Anode fabrication procedure involved the blending of two-kilogram samples of aggregate with pitch for 30 minutes in a 3.8 litre (1 gal.) sigma-blade mixer heated at 140°C. Green specimens, 50.8 mm (2 in.) in diameter and approximately 150 mm (~6 in.) long, were formed in a mold preheated to 140°C by application of 27.6 MPa (4000 psi) pressure. Green specimens were packed in calcined coke and baked under a nitrogen purge at an upheat rate of 25°C/hr to 1135°C and held at that temperature for 10 hours.

Anode green and baked apparent densities and volume change during baking were measured. Since the green apparent densities were not particularly informative, they were not included in this report.

To determine resistance to mechanical stress, flexural strength was measured using a room temperature, four-point loading test (ASTM C78-C4). Most values reported are averages of four determinations. Although stresses in various cases may in fact be tensile, compressive or shear, it is believed that differences among various carbons would be in about the same relative order of the flexural strengths. In some cases measurements also were made at 600°C, a typical temperature for the top portion of an anode. Deflections occurring before cracking were made using an LVDT gage head.

Thermal shock susceptibility was measured using a test similar in principle to that described by Brown and Rhedey (1). This test involves heating the central portion of a thin disc and recording time until cracking. Since Brown and Rhedey did not report their experimental conditions, suitable conditions were derived by trial and error (and are shown in Figure 1). For this reason, values reported in this work do not correlate with those of Brown and Rhedey. Values reported are averages of 6-8 tests.

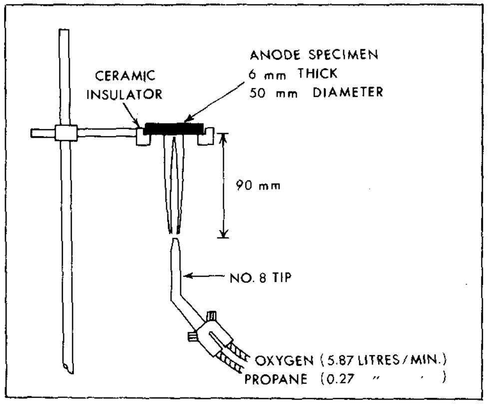

Figure 1. Schematic of Anode Thermal Shock Resistance Test

Analysis has shown (3) that within the heated central part of the disc there are radial and tangential compressive stresses; at points outside the heated part there are both compression and tensive stresses; and that at the edge of the heated portion there is a maximum shear stress.

Specific Experiments and Results

With the cokes characterized in Table I, anodes were produced using maximum bulk density compositions [determined as described in (4)] with 16, 18 and 20 percent pitch. Thermal shock test result for each of the cokes at the optimum pitch level was correlated with coke real density (Figure 2). Since real density and crystallite height were closely related (except for coal tar pitch Coke "D"), an equivalent correlation with crystallite height could be made also.

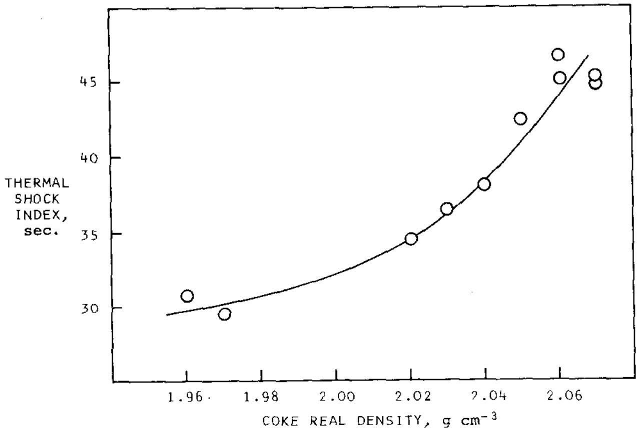

Figure 2. Effect of Coke Real Density on Anode Thermal Shock Index

In contrast to electrical resistivity and excess consumption, which according to published literature generally decrease with increasing coke bulk density (1,5), thermal shock resistance was dependent on coke bulk density only to the extent that most of the higher bulk density cokes had the lower real densities. It was not clear whether this was because low bulk density cokes, which tend to be more anisotropic, densify more readily as suggested by Whittaker, Miller, and Fritz (6), or whether most of the lower bulk density cokes were merely calcined at higher temperatures.

It is possible to estimate coke calcination temperature by heating samples to successively higher temperatures until real density (or crystallite height) begins to increase. The temperature at which the curve breaks represents the original calcination temperature. This procedure was carried out for the ten cokes.

Figure 3 shows that within the group of cokes tested, real density appears to be primarily affected by calcination temperature. It is likely that many calciners use electrical resistivity as a measure of adequate calcination so that high bulk density cokes, which have inherently lower resistivities, will frequently be calcined to lower temperatures than lower bulk density cokes. Therefore, while high bulk density cokes may give good electrical resistivities and give low consumption values at calcination temperatures well below those required for low bulk density cokes, higher coke calcination temperatures should be considered if thermal shock type cracking problems occur at a particular smelter.

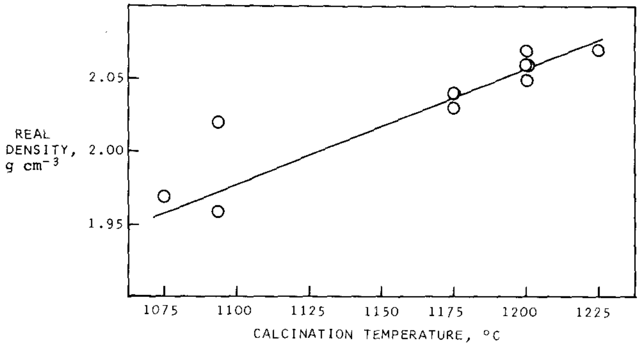

Figure 3. Relationship Between Coke Calcination Temperature and Real Density

Although the reason for the direct correlation between coke real density (or crystallite height) and anode thermal shock resistance was not determined, it can be postulated that because cokes with high real density have more microporosity, it enables them to relieve thermal stresses more easily. The larger, more widely separated pores, which mostly determine coke bulk density, may not be as effective in relieving these stresses.

Unfortunately, many of the specimens prepared from these cokes were consumed in developing the thermal shock test procedure, so it was not possible to run a complete flexural strength test series on these samples. However, flexural strengths on anodes from four of the cokes, representing a range in bulk density, were determined as part of the test series reported below. Maximum flexural strengths were: Coke "A", 11.7 MPa; Coke "G", 10.2 MPa; Coke "H", 9.5 MPa; and Coke "J", 9.6 MPa. Flexural strength was roughly proportional to coke bulk density, although maximum strengths with the two lowest density cokes were about equal.

The effects of formulation variables on anode cracking tendency were also studied. Initially, a medium bulk density coke, Coke "G", was selected. Sizing and pitch level were varied over a broad range so that trends could be determined easily. Table II gives the sizings used in this study and results are given in Figure 4. As bulk densities of the aggregates increased, maximum baked apparent densities increased. This correlated with an increase in both maximum flexural strength and maximum thermal shock resistance.

Table II. Aggregate Sizings used in Cracking Test Studies with Coke "G"

Tyler Mesh Fraction	Screen Openings, mm	Wt. % of Fraction Sizing a	Sizing b	Sizing c	Sizing d
+8	+2.38	9	10	5	-
-8+14	-2.38+1.19	26	23	19	-
-14+28	-1.19+0.60	11	10	6	14
-28+48	-0.60+0.30	8	22	20	52
-48+100	-0.30+0.15	11	15	30	28
-100+200	-0.15+0.07	13	10	10	4
-200	-0.07	22	10	10	2

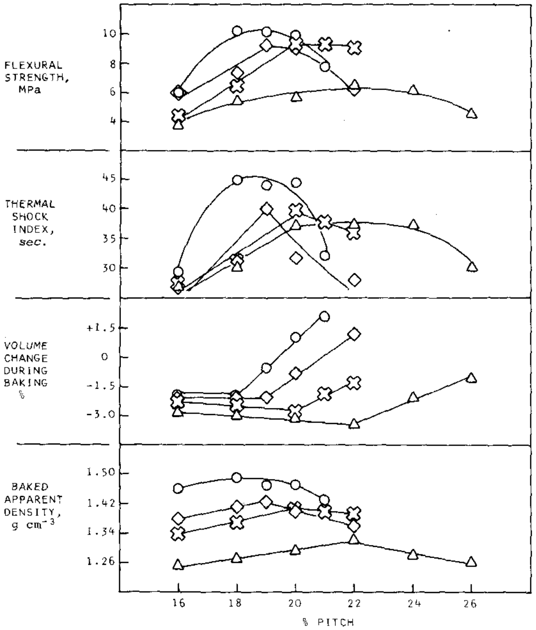

Figure 4. Effects of Aggregate Sizing and Pitch Level on Anode Properties - Coke "G" (○, Sizing a; ◇, Sizing b; ⌘, Sizing c; △, Sizing d)

The binder content which resulted in the maximum baked apparent density was optimum for flexural strength and thermal shock resistance. This was the level at which there was a change in slope of the volume change during baking vs. pitch percent curve. This is obviously the point at which pitch fills coke pores and interstices between coke particles to the maximum extent possible, while still allowing enough free space to accept the expanding pitch on initial heating during baking. At higher pitch levels, inadequate free space remains to accept the thermally expanding pitch and coke particles are pushed apart. At pitch levels not much above the optimum, net shrinkage still occurs because of shrinkage of the pitch network during coking, and properties generally are not much below the optimum.

It should be noted that with these formulation changes there is no unique correlation between baked apparent density and flexural strength or thermal shock resistance, even though such a correlation exists when only changing pitch content while keeping coke and aggregate constant. This is shown in Figure 5. Apparently, quality and quantity of the binder coke are the most important factors in anode strength. Cracks most often propagate through the binder coke or at the binder coke - aggregate coke interface. Increase in baked apparent density, attained by increasing the aggregate bulk density of a given coke by sizing changes, is not particularly beneficial if the pitch level is so low that the contact area between binder coke and aggregate coke particles is low or the pitch level so high that thick, porous binder coke bridges are formed.

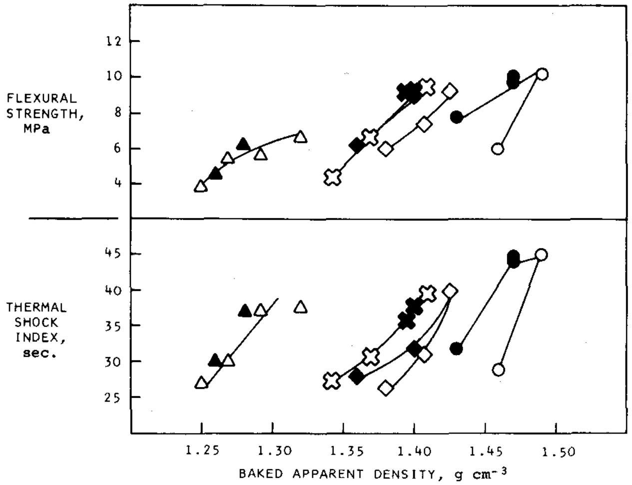

Figure 5. Relationships Between Anode Baked Apparent Density and Cracking Tendencies (○, Sizing a; ◇, Sizing b; ✣, Sizing c; △, Sizing d - Solid Figures Indicate Greater than Optimum % Pitch

Although these formulation experiments provided useful guidelines for increasing anode crack resistance, additional experiments using relatively smaller differences in aggregate sizing more typical of those used in practice (Table III) and using a high, medium and low bulk density coke (Cokes "B", "H", and "J") were also conducted. Results are shown in Figures 6, 7 and 8. Although correlations among coke density, aggregate sizing, pitch content, anode thermal shock resistance, and flexural strength are not as straightforward as desired, some generalizations can be made. With the coarsest sizing, both thermal shock resistance and flexural strength tended to maximize

Table III. Aggregate Sizings used in Cracking Test Studies with Cokes "B", "H", and "J"

Tyler Mesh Fraction	Screen Openings, mm	Wt. % of Fraction Sizing 1	Sizing 2	Sizing 3
+8	+2.38	5	10	15
-8+14	-2.38+1.19	15	19	20
-14+28	-1.19+0.60	18	14	15
-28+48	-0.60+0.30	11	12	11
-48+100	-0.30+0.15	10	10	9
-100+200	-0.15+0.07	15	14	14
-200	-0.07	26	21	16

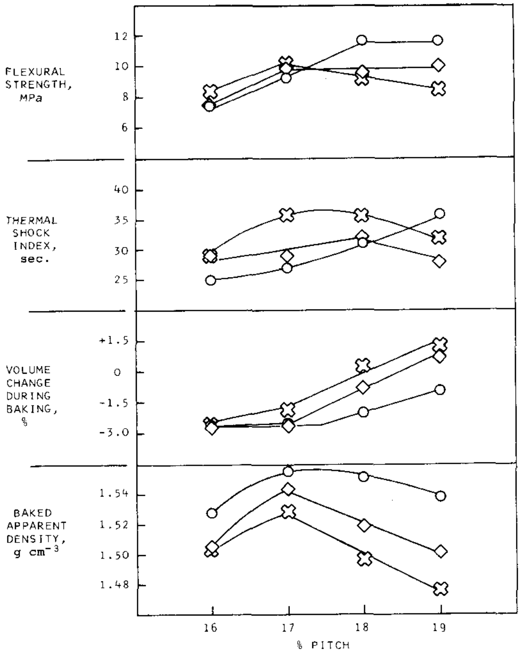

Figure 6. Effects of Aggregate Sizing and % Pitch on Anode Properties - Coke "B" (○, Sizing 1; ◇, Sizing 2; ✣, Sizing 3)

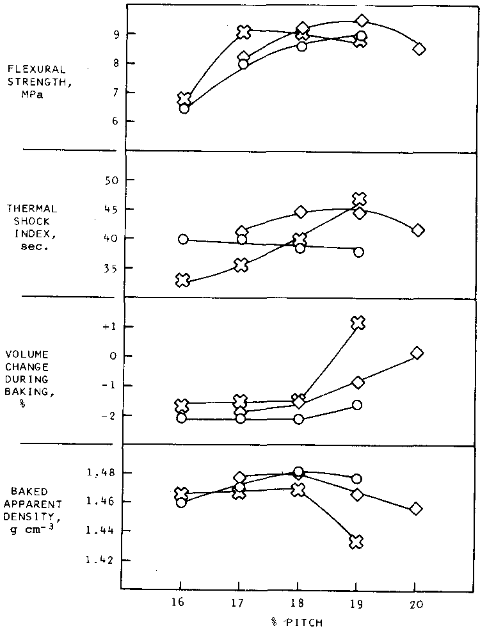

Figure 7. Coke "H"

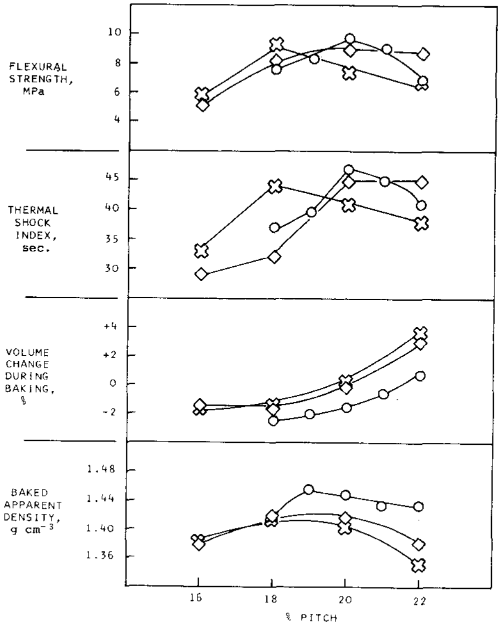

Figure 8. Coke "J"

Effects of Aggregate Sizings and % Pitch on Anode Properties
(○, Sizing 1; ◇, Sizing 2; ✠, Sizing 3)

at the pitch level resulting in the maximum baked apparent density (with thermal shock resistance for Coke "H" an obvious exception). With the medium sizing, there was some tendency toward maximization of these properties at pitch levels higher than that producing the maximum baked apparent density. With the fine sizing these properties nearly always optimized at pitch levels higher than that producing the maximum baked apparent density. The reason for this is not obvious.

There is no clear-cut trend of any sizing resulting in consistently high thermal shock resistance and flexural strength even though the fine sizing usually resulted in the highest baked apparent density. Since there was usually no increase in maximum crack resistance using the medium and fine sizings and since maximum crack resistance may not be attained at the pitch level producing the highest baked apparent density for these sizings, it appears advantageous to use a coarser sizing when cracking is a problem. It is unlikely, in any case, that industrial anodes having pitch contents above that required to produce the maximum baked apparent density could be made without problems.

Results for these cokes, along with Coke "G", indicate that maximum flexural strength (optimum sizing and pitch content for each coke) is roughly proportional to coke bulk density; but, thermal shock resistance was not related to coke bulk density, as mentioned earlier.

In some cases anode strength may not be as important as ability to deform under an applied load, through localized crushing or general flexibility of the anode. An example would be pressure exerted by a thermally expanding stub. An anode which is somewhat flexible might resist cracking more than a weaker but less flexible (lower modulus) anode. Hence, deflections occurring before breakage were measured for a number of specimens during the flexural strength test. These are shown in Figure 9 as a function

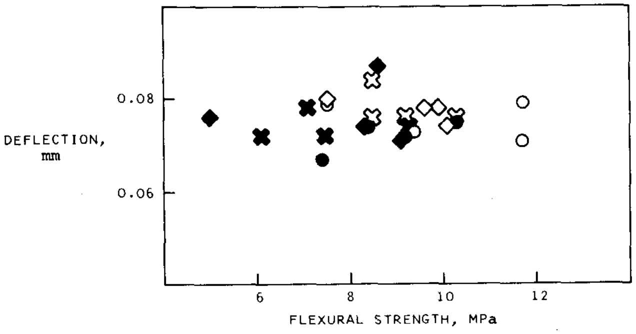

Figure 9. Specimen Deflection Before Breaking During Flexural Strength Test (○, Sizing 1; ◇, Sizing 2; ✠, Sizing 3 - Open Figures, Coke "B", Solid Figures, Coke "J")

of flexural strength. For the specimens tested, deflection appears to be independent of coke bulk density, aggregate sizing and flexural strength. Apparently, strength would be the dominant factor even in the case described above.

It is well known that carbons and graphites increase in strength with increasing temperature. Flexural strengths of some specimens were measured at 600°C (a typical temperature for the top of an anode) to determine whether percent strength increase with temperature is a constant. If strength increase is affected by coke or aggregate factors, this would tend to make the room temperature data less useful. Results are shown in Figure 10. Although percent strength increase was not constant, it did not depend much on specific formulation variables, but rather upon absolute strength. That is, the higher the room temperature strength, the greater percent increase in strength (up to about 33%) at 600°C. Thus, differences in room temperature strengths are not only valid at 600°C but are magnified.

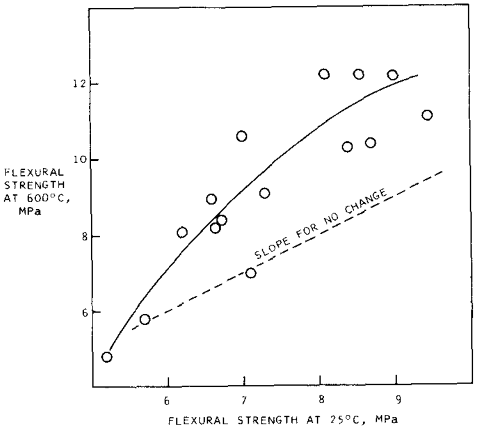

Figure 10. Relationship Between Flexural Strengths of Specimens at 25°C and 600°C

Summary

1. Thermal shock resistances of bench scale anodes made using cokes typical of those used in prebaked anode manufacture increased with increasing coke real density (or crystallite height).
2. Since, for the cokes tested, real density correlated with estimated coke calcination temperature, it can be implied that anode thermal shock resistance increases with coke calcination temperature over a typical calcination temperature range.
3. Flexural strengths of specimens correlated roughly with coke bulk density.
4. With coarse sizings, a binder level resulting in maximum baked apparent density resulted in maximum thermal shock resistance and flexural strength.
5. Even though thermal shock resistance and flexural strength were a function of baked apparent density for a given coke and aggregate sizing, there was no overall correlation of these properties with baked apparent density when sizing was altered.
6. With a fine aggregate sizing, thermal shock resistance and flexural strength maximized at pitch levels greater than that producing maximum baked apparent density, so maximum values could probably not be attained in commercial anodes.
7. In the flexural strength test, there was no apparent correlation of deflection of specimens before breaking with strength, aggregate sizing, pitch level, or coke bulk density.
8. Differences among flexural strengths of specimens at room temperature were increased at 600°C, a typical temperature for the top of an anode.

Conclusions

1. The above results suggest that thermal shock induced cracking of prebaked anodes can be reduced by specifying high coke real density, using an aggregate sizing on the coarse side of the practical range, and by selecting the pitch content which gives the maximum baked apparent density.
2. The above results suggest that to increase resistance of prebaked anodes to cracking from mechanical stress, a high coke bulk density should be specified, aggregate sizing should be on the coarse side of the practical range, and the pitch content giving the maximum baked apparent density should be used. Cracking originating from near the top of the anode; i.e., at the stub hole, may be reduced by conditions which result in a higher anode temperature for a given amount of stress, since strength increases with temperature.

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