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SAG CONTROL OF ISOPIPES USED IN MAKING
SHEET GLASS BY THE FUSION PROCESS

FIELD OF THE INVENTION

This invention relates to isopipes used in the production of sheet glass by the fusion process and, in particular, to techniques for controlling the sag which such isopipes exhibit during use.

BACKGROUND OF THE INVENTION

A. The Fusion Process

The fusion process is one of the basic techniques used in the glass making art to produce sheet glass. See, for example, Varshneya, Arun K., "Flat Glass," Fundamentals of Inorganic Glasses, Academic Press, Inc., Boston, 1994, Chapter 20, Section 4.2., 534-540. Compared to other processes known in the art, e.g., the float and slot draw processes, the fusion process produces glass sheets whose surfaces have superior flatness and smoothness. As a result, the fusion process has become of particular importance in the production of the glass substrates used in the manufacture of liquid crystal displays (LCDs).

The fusion process, specifically, the overflow downdraw fusion process, is the subject of commonly assigned U.S. Patents Nos. 3,338,696 and 3,682,609, to Stuart M. Dockerty, the contents of which are incorporated herein by reference. A schematic drawing of the process of these patents is shown in FIG. 1. As illustrated therein, the system includes a supply pipe 9 which provides molten glass to a collection trough 11 formed in a refractory body 13 known as an "isopipe."

Once steady state operation has been achieved, molten glass passes from the supply pipe to the trough and then overflows the top of the trough

on both sides, thus forming two sheets of glass that flow downward and then inward along the outer surfaces of the isopipe. The two sheets meet at the bottom or root 15 of the isopipe, where they fuse together into a single sheet. The single sheet is then fed to drawing equipment (represented 5 schematically by arrows 17), which controls the thickness of the sheet by the rate at which the sheet is drawn away from the root. The drawing equipment is located well downstream of the root so that the single sheet has cooled and become rigid before coming into contact with the equipment.

As can be seen in FIG. 1, the outer surfaces of the final glass sheet do 10 not contact any part of the outside surface of the isopipe during any part of the process. Rather, these surfaces only see the ambient atmosphere. The inner surfaces of the two half sheets which form the final sheet do contact the isopipe, but those inner surfaces fuse together at the root of the isopipe and are thus buried in the body of the final sheet. In this way, the superior 15 properties of the outer surfaces of the final sheet are achieved.

As is evident from the foregoing, isopipe 13 is critical to the success of the fusion process. In particular, the dimensional stability of the isopipe is of great importance since changes in isopipe geometry affect the overall success of the process. See, for example, Overman, U.S. Patent No. 20 3,437,470, and Japanese Patent Publication No. 11-246230.

Significantly, the conditions under which the isopipe is used make it susceptible to dimensional changes. Thus, the isopipe must operate at elevated temperatures on the order of 1000°C and above. Moreover, in the case of the overflow downdraw fusion process, the isopipe must operate at 25 these elevated temperatures while supporting its own weight as well as the weight of the molten glass overflowing its sides and in trough 11, and at least some tensional force that is transferred back to the isopipe through the fused glass as it is being drawn. Depending on the width of the glass sheets that are to be produced, the isopipe can have an unsupported length 30 of 1.5 meters or more.

To withstand these demanding conditions, isopipes 13 have been manufactured from isostatically pressed blocks of refractory material (hence the name "iso-pipe"). In particular, isostatically pressed zircon refractories have been used to form isopipes for the fusion process. As
5 known in the art, zircon refractories are materials composed primarily of ZrO_2 and SiO_2 , e.g., in such materials, ZrO_2 and SiO_2 together comprise at least 95 wt.% of the material, with the theoretical composition of the material being $ZrO_2 \cdot SiO_2$ or, equivalently, $ZrSiO_4$. Even with such high performance materials, in practice, isopipes exhibit dimensional changes
10 which limit their useful life. In particular, isopipes exhibit sag such that the middle of the unsupported length of the pipe drops below its outer supported ends. The present invention is concerned with controlling such sag.

A primary contributor to the sag of an isopipe is the creep rate
15 $\dot{\epsilon} = ds/dt$ of the material from which it is made. As known in the art, for many materials, creep rate as a function of applied stress σ can be modeled by a power law expression of the following form:

$$\dot{\epsilon} = A\sigma^n \exp(Q/T) \quad (1)$$

where T is temperature and A, n, and Q are material dependent constants.
20 See Kingery et al., "Plastic Deformation, Viscous Flow, and Creep," Introduction to Ceramics, 2nd edition, John Wiley & Sons, New York, 1976, 704-767 and, in particular, equation 14.9. Being the time derivative of strain, the units of creep rate are length/length/time. Because in equation (1) creep rate varies as stress raised to a power, i.e., σ^n , the use of equation
25 (1) will be referred to herein as the "power law model."

Lowering the creep rate of the material used to make an isopipe results in less sag during use. As discussed in detail below, in accordance with certain aspects of the invention it has been found that the sag of an isopipe can be reduced by forming the isopipe from an isostatically pressed
30 zircon refractory having a titania (TiO_2) content which is greater than 0.2 wt.% and less than 0.4 wt.%, e.g., a TiO_2 content of approximately

0.3 wt.%. In particular, it has been found that such a zircon refractory exhibits a lower mean creep rate than zircon refractories used in the past to from isopipes and having a titania content of about 0.1 wt.%.

In addition, it has also been found that controlling the titania content of a zircon refractory to be within the above range significantly enhances the usefulness of the power law model of equation (1) in modeling the sag of isopipes during use. This enhanced usefulness results from improved 95% confidence intervals for the mean creep rates predicted by the model when equation (1) is evaluated for a particular set of σ, T values. Such improved 95% confidence intervals, in turn, mean that the sag which an isopipe will exhibit during use can be more accurately modeled using, for example, a finite element or other modeling technique. More accurate modeling greatly enhances the ability to develop improved isopipe designs since numerous designs can be evaluated theoretically with only the best candidates being selected for actual construction and testing.

B. Zircon Refractories

As indicated above, the present invention relates to isopipes composed of a zircon refractory having a titania concentration within specified limits. Corhart Refractories Corporation (Louisville, Kentucky) offers a number of zircon refractories containing varying amounts of TiO_2 . For example, Corhart's ZS-835 product is specified to contain 0.2 wt.% TiO_2 , its ZS-835HD product 0.4 wt.%, its Zircon 20 product 0.7 wt.%, and its ZS-1300 product 1.2 wt.%.

As a raw material, zircon can have varying amounts of titania. For example, U.S. Patent No. 2,752,259 reports that the zircon used in its examples had 0.34 wt.% TiO_2 , while the zircon used in U.S. Patent No. 3,285,757 had 0.29 wt.% TiO_2 . U.S. Patents Nos. 3,347,687 and 3,359,124 each describe zircons having TiO_2 concentrations of 0.2 wt.%. In addition to being naturally present in zircon as a raw material, TiO_2 can also be a component of clays used in producing zircon refractories. See U.S. Patents Nos. 2,746,874 and 3,359,124.

Other discussions of the use of titania in zircon products can be found in Goerenz et al., U.S. Patent No. 5,407,873 which discloses (1) the use of phosphorus compounds to improve the corrosion resistance of zirconium silicate bricks and (2) the use of titanium dioxide as a sintering aid in the manufacture of such bricks. Although the patent states that sintering can be improved by adding between 0.1 wt.% and 5 wt.% of titanium dioxide, all of the examples of the patent use more than 1 wt.% of titanium dioxide and the patent's preferred composition consists of 98 wt.% zirconium silicate, 1.5 wt.% titanium dioxide, and 0.5 wt.% of a phosphorous compound.

Wehrenberg et al., U.S. Patent No. 5,124,287 relates to the use of zirconia in particle form to improve the thermal shock resistance of zircon refractories. Titania is employed to enhance grain growth during sintering. The patent claims titania concentrations between 0.1 wt.% and 4 wt.%. The preferred titania concentration is 1 wt.%, and when blistering is a problem, only 0.1 wt.% titania is used. The patent states that "grog" having a titania concentration of 0.2 wt.% was used as a starting material for some of its examples.

Significantly, none of the foregoing disclosures regarding the use of titania in zircons relates to employing titania concentration as a means to control the creep rate of a zircon refractory, or to enhance the ability of a power law model to represent the material, or to achieve the ultimate goal of reducing the sag of an isopipe made of a zircon refractory.

SUMMARY OF THE INVENTION

In view of the foregoing, it is an object of this invention to provide improved isopipes for use in the fusion process. More particularly, it is an object of the invention to provide isopipes that exhibit less sag than existing isopipes.

To achieve the foregoing and other objects, the invention in accordance with a first aspect provides isopipes which comprise a zircon refractory that exhibits a lower creep rate than the zircon refractories previously used to produce isopipes.

In accordance with a second aspect, the invention provides isopipes which comprise a zircon refractory that in comparison to zircon refractories previously used to produce isopipes, has a creep rate that can be modeled more accurately by a power law model.

5 In accordance with a third aspect, the invention provides isopipes comprising a body having a configuration adapted for use in a fusion process, said body comprising a zircon refractory which purposely comprises TiO_2 at a concentration greater than 0.2 wt.% and less than 0.4 wt.%, preferably greater than 0.25 wt.% and less than 0.35 wt.%, and most
10 preferably about 0.3 wt.%.

In accordance with a fourth aspect, the invention provides isopipes comprising a body having a configuration adapted for use in a fusion process, said body comprising a zircon refractory which has a mean creep rate (MCR) at 1180°C and 250 psi of less than 0.7×10^{-6} inches/inches/hour,
15 preferably less than 0.6×10^{-6} inches/inches/hour, and most preferably less than 0.5×10^{-6} inches/inches/hour, where the MCR is determined using a power law model, i.e., a power law model fit to experimental data.

In accordance with this fourth aspect, the zircon refractory also preferably has a MCR at 1180°C and 1000 psi of less than 5×10^{-6}
20 inches/inches/hour and more preferably less than 3×10^{-6} inches/inches/hour, where again the MCR is determined using a power law model.

In accordance with a fifth aspect, the invention provides isopipes comprising a body having a configuration adapted for use in a fusion
25 process, said body comprising a zircon refractory which has a MCR at 1180°C and 250 psi and a 95 percent confidence band (CB) for said MCR such that the CB to MCR ratio is less than 0.5, the MCR and the CB both being determined using a power law model. In accordance with these aspects of the invention, the CB to MCR ratio at 1180°C and 1000 psi is
30 also preferably less than 0.5, where again the MCR and the CB values used

to calculate the CB to MCR ratio at said temperature and stress level are determined using a power law model.

In accordance with a sixth aspect, the invention provides a method for reducing the sag of an isopipe used in a fusion process that produces
5 glass sheets comprising forming said isopipe from a zircon refractory which purposely comprises TiO_2 at a concentration greater than 0.2 wt.% and less than 0.4 wt.%, preferably greater than 0.25 wt.% and less than 0.35 wt.%, and most preferably about 0.3 wt.%.

The above first through sixth aspects of the invention can be used
10 separately or in all possible combinations. For example, the compositional limitations of the third and sixth aspects of the invention (including the base, preferred, and most preferred values of those limitations) can be combined with the mean creep rate limitations of the fourth aspect of the invention (including the base, preferred, and most preferred values of those
15 limitations) and/or with the CB to MCR ratio limitations of the fifth aspect of the invention (including the base and preferred pressure values of those limitations). Similarly, the mean creep rate limitations of the fourth aspect of the invention (including the base, preferred, and most preferred values of those limitations) can be combined with CB to MCR ratio limitations of the
20 fifth aspect of the invention (including the base and preferred pressure values of those limitations).

As used in this specification and in the claims, the term "isopipe" means any sheet forming delivery system used in a fusion process which produces flat glass wherein at least a part of the delivery system comes into
25 contact with the glass just prior to fusion, irrespective of the configuration or the number of components making up the delivery system. Also, the MCR and CB values are determined using standard statistical techniques for calculating such values from the fit of an equation such as the power law model to measured data. See, for example, Draper et al., Applied
30 Regression Analysis, John Wiley & Sons, New York, 1981, 193-212.

Further, the word "purposely" when used in connection with TiO_2 concentrations means that the TiO_2 concentration is intentionally selected to control isopipe sag and is not merely a TiO_2 concentration which one or more zircons (including zircons for making isopipes) may have had as a
5 result of compositional variations without being the result of a conscious intention to control isopipe sag and/or to improve the ability of a power law model to represent the creep rate of zircon used in an isopipe.

Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily
10 apparent to those skilled in the art from that description or recognized by practicing the invention as described herein. It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention, and are intended to provide an overview or framework for understanding the nature and
15 character of the invention as it is claimed. The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate various aspects of the invention, and together with the description serve to explain the principles and operation of the invention.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing illustrating a representative construction for an isopipe for use in an overflow downdraw fusion process for making flat glass sheets.

Figures 2A and 2B are three dimensional plots showing
25 experimentally measured creep rate as a function of temperature and stress for zircon specimens having TiO_2 concentrations of 0.12 wt.% and 0.30 wt.%, respectively.

Figures 3A and 3B are plots illustrating the differences in creep rate variability at a temperature of 1180°C for 0.12 wt.% TiO_2 versus 0.30 wt.%
30 TiO_2 for applied stresses of 250 psi and 1000 psi, respectively.

DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the present invention relates to the use of zircon refractories to produce isopipes for use in a fusion process where the zircon refractory has a TiO_2 content greater than 0.2 wt.% and less than 0.4 wt.%.

5 Such a TiO_2 content causes the isopipe to exhibit reduced sag as a result of the refractory having a lower mean creep rate than zircon refractories currently used in the art. For example, the zircon refractory can have a mean creep rate at 1180°C and 250 psi substantially less than 0.5×10^{-6} inches/inches/hour.

10 In addition, such a TiO_2 content also causes the refractory to have a 95% confidence band (CB) for said mean creep rate (MCR) which is less than 50% of the mean creep rate, i.e., $\text{CB/MCR} < 0.5$. Such a confidence band reduces the chances that the zircon refractory of a particular isopipe will have an abnormally high creep rate and thus cause the isopipe to have
15 a short lifetime as a result of exhibiting unacceptable sag prematurely.

The TiO_2 content of a zircon refractory can be determined using various techniques known in the art. For example, the content can be determined by means of an X-ray fluorescence analysis (XRF). The titania content of the refractory can be adjusted so that the final product has the
20 desired TiO_2 content by incorporating TiO_2 as needed in the batch materials used to prepare the refractory. Thereafter, the refractory can be prepared in accordance with techniques currently known in the art or with improved techniques which may be developed in the future.

Similarly, isopipes can be prepared from the zircon refractories of the
25 invention using techniques currently known in the art or with improved techniques which may be developed in the future. Typically, the isopipe will be prepared by being machined from a single block of the zircon refractory, although other approaches can be used if desired.

Without intending to limit it in any manner, the present invention
30 will be more fully described by the following examples.

Lots of zircon refractories containing 0.12 wt.% or 0.30 wt.% TiO_2 were obtained from Corhart Refractories Corporation (Louisville, Kentucky). Each lot represented a separate firing and typically included multiple blocks of material of suitable dimensions to produce an isopipe, i.e., the blocks had lengths greater than 1.5 meters.

Creep rate tests were performed on 117 specimens taken from blocks having 0.12 wt.% TiO_2 and 142 specimens taken from blocks having 0.30 wt.% TiO_2 . A three point flexure technique was used to determine creep rates in which a bar of the material being tested was supported at its ends and loaded at its center. The applied stress in pounds per square inch (psi) was determined in accordance with conventional procedures as set forth in ASTM C-158. In particular, applied stress σ was determined from the relation:

$$\sigma = 3 \cdot \text{AL} \cdot \text{SS} / (2 \cdot \text{SW} \cdot \text{SH}^2)$$

where AL = applied load, SS = support span, SW = specimen width, and SH = specimen height.

The bar was heated and its flexure as a function of time was measured. A midspan deflection rate was obtained by calculating the slope of the resulting deflection versus time plot once steady state conditions for the particular load and temperature had been reached. In particular, the midspan deflection rate was determined for the "secondary creep" portion of the strain versus time curve. See, for example, the Kingery et al. text cited above at pages 707-709.

Creep rates $\dot{\epsilon}$ were then obtained from the relation:

$$\dot{\epsilon} = \text{DR} \cdot 2 \cdot \text{SH} / \text{SS}^2$$

where SH and SS are as defined above and DR = midspan deflection rate.

FIG. 2A and FIG. 2B are three dimensional plots of the creep rate values obtained in this way for the 0.12 wt.% TiO_2 and 0.30 wt.% TiO_2 specimens, respectively. The reduction in the scatter of the data achieved by the change in TiO_2 concentration is immediately evident from these figures. In terms of producing isopipes which will have repeatable creep

properties, the data of these figures show that a zircon refractory having a TiO_2 content of around 0.3 wt.% is clearly much better than one having a TiO_2 content around 0.1 wt.%.

The power law model of equation (1) was fit to the data of FIG. 2A and to that of FIG. 2B using a commercial data analysis package, namely, "TableCurve 3D: Automated Surface Fitting and Equation Discovery," Version 3.0 for Windows® 95 & NT, software and documentation, SPSS Inc., Chicago, 1997 (hereinafter the "TABLE CURVE 3D program"). The values of the material dependent constants A, n, and Q obtained in this way for the two cases are set forth in Table 1.

Using these constants and the TABLE CURVE 3D program, mean creep rates and 95% confidence bands were determined for a temperature of 1180°C and a stress of 250 psi, which are representative of the temperatures and stress levels which an isopipe will typically experience during use. The results of this analysis are shown in FIG. 3A.

Two important facts are evident from this figure. First, the mean creep rate has been substantially reduced as a result of the increase in TiO_2 content from 0.12 wt.% to 0.30 wt.%. This means that isopipes composed of zircon refractories having higher TiO_2 than previously used will exhibit less sag during use, a highly desirable result. Moreover, the size of the 95% confidence band has also been substantially reduced by the increase in TiO_2 content. This means that an individual isopipe made from an individual block of a zircon refractory is more likely to have its creep rate closer to the predicted mean creep rate when the TiO_2 content of the material is increased than when it is not increased, another highly desirable result since predictability in a manufacturing setting makes for more efficient planning and operation.

To further demonstrate the controlling effect which TiO_2 content has on creep rate, mean creep rates and 95% confidence bands were also determined for a stress of 1000 psi, again using the constants of Table 1 and the TABLE CURVE 3D program. The results are shown in FIG. 3B.

The reduction in mean creep rate achieved by increasing the TiO_2 content is even greater at this higher stress level.

- Table 2 summarizes the results of using the TABLE CURVE 3D program to determine mean creep rates and 95% confidence bands for the data of FIG. 2. Zircon refractories having a TiO_2 content above and below the 0.3 wt.% value used to generate this data will exhibit similar MCR and CB values to those shown in Table 2. In particular, reduced MCR and CB/MCR values compared to previously used zircon refractories are achieved when the TiO_2 content of the refractory is greater than 0.2 wt.%. The improved performance continues as the TiO_2 content is increased above 0.3 wt.%. However, oxygen blisters can be generated at the isopipe/glass interface when the TiO_2 content of the zircon refractory reaches about 0.4 wt.%. Thus, in accordance with the invention, the TiO_2 content of the refractory should be above 0.2 wt.% but below 0.4 wt.%. Although specific embodiments of the invention have been discussed, a variety of modifications to those embodiments which do not depart from the scope and spirit of the invention will be evident to persons of ordinary skill in the art from the disclosure herein. The following claims are intended to cover the specific embodiments set forth herein as well as such modifications, variations, and equivalents.

TABLE 1

TiO ₂ (wt.%)	A	n	Q
0.12	1.04×10^{12}	1.56	-73302
0.30	1.20×10^{14}	1.33	-79038

TABLE 2

Example	TiO ₂ (wt.%)	T (°C)	σ (psi)	MCR (10^{-6} in/in/hr)	CB (10^{-6} in/in/hr)	CB/MCR
1	0.12	1180	250	0.7197	0.5163 to 1.003	0.6763
2	0.30	1180	250	0.4340	0.3500 to 0.5390	0.4355
3	0.12	1180	1000	6.296	4.811 to 8.240	0.5446
4	0.30	1180	1000	2.730	2.210 to 3.380	0.4286

MCR = mean creep rate

CB = 95% confidence band for the MCR

What is claimed is :

1. An isopipe comprising a body having a configuration adapted for use in a fusion process, said body comprising a zircon refractory which comprises TiO_2 at a concentration greater than 0.2 wt.% and less than 0.4 wt.%.
2. The isopipe of Claim 1 wherein the zircon refractory comprises TiO_2 at a concentration greater than 0.25 wt.% and less than 0.35 wt.%.
3. The isopipe of claim 1 wherein the zircon refractory comprises TiO_2 at a concentration of about 0.3 wt.%.
4. The isopipe of claim 1 wherein the zircon refractory has a mean creep rate at 1180°C and 250 psi of less than 0.5×10^{-6} inches/inch/hour, where the mean creep rate is determined using a power law model.
5. The isopipe of claim 1 wherein the zircon refractory has a mean creep rate at 1180°C and 1000 psi of less 3.0×10^{-6} inches/inch/hour, where the mean creep rate is determined using a power law model.
6. The isopipe of claim 1 wherein the zircon refractory has a mean creep rate (MCR) at 1180°C and 250 psi and a 95 percent confidence band (CB) for said mean creep rate such that the CB to MCR ratio is less than 0.5, said mean creep rate and said 95 percent confidence band being determined using a power law model.
7. The isopipe of claim 1 wherein the zircon refractory has a mean creep rate (MCR) at 1180°C and 1000 psi and a 95 percent confidence band (CB) for said mean creep rate such that the CB to MCR ratio is less than 0.5, said mean creep rate and said 95 percent confidence band being determined using a power law model.

8. An isopipe comprising a body having a configuration adapted for use in a fusion process, said body comprising a zircon refractory which: (i) comprises TiO_2 at a concentration greater than 0.2 wt.% and (ii) has a mean creep rate at 1180°C and 250 psi of less than 0.7×10^{-6} inches/inch/hour, where the mean creep rate is determined using a power law model.

9. The isopipe of claim 8 wherein the mean creep rate is less than 0.6×10^{-6} inches/inches/hour.

10. The isopipe of claim 8 wherein the mean creep rate is less than 0.5×10^{-6} inches/inches/hour.

11. The isopipe of claim 8 wherein the mean creep rate (MCR) at 1180°C and 250 psi has a 95 percent confidence band (CB) such that the CB to MCR ratio is less than 0.5, said 95 percent confidence band being determined using a power law model.

12. The isopipe of claim 8 wherein the zircon refractory has a mean creep rate at 1180°C and 1000 psi of less than 5×10^{-6} inches/inches/hour, where the mean creep rate is determined using a power law model.

13. The isopipe of claim 12 wherein the mean creep rate at 1180°C and 1000 psi is less than 3×10^{-6} inches/inches/hour.

14. The isopipe of claim 12 wherein the mean creep rate (MCR) at 1180°C and 1000 psi has a 95 percent confidence band (CB) such that the CB to MCR ratio is less than 0.5, said 95 percent confidence band being determined using a power law model.

15. An isopipe comprising a body having a configuration adapted for use in a fusion process, said body comprising a zircon refractory which: (i) comprises TiO_2 at a concentration greater

than 0.2 wt.% and (ii) has a mean creep rate (MCR) at 1180°C and 250 psi and a 95 percent confidence band (CB) for said mean creep rate such that the CB to MCR ratio is less than 0.5, the MCR and the CB both being determined using a power law model.

16. The isopipe of claim 15 wherein the zircon refractory has a mean creep rate (MCR) at 1180°C and 1000 psi and a 95 percent confidence band (CB) for said mean creep rate such that the CB to MCR ratio is less than 0.5, the MCR and the CB both being determined using a power law model.

17. A method for reducing the sag of an isopipe used in a fusion process that produces glass sheets comprising forming said isopipe from a zircon refractory which comprises TiO_2 at a concentration greater than 0.2 wt.% and less than 0.4 wt.%.

18. The method of claim 17 wherein the zircon refractory comprises TiO_2 at a concentration greater than 0.25 wt.% and less than 0.35 wt.%.

19. The method of claim 17 wherein the zircon refractory comprises TiO_2 at a concentration of about 0.3 wt.%.

20. The method of claim 17 wherein the zircon refractory has a mean creep rate at 1180°C and 250 psi of less than 0.5×10^{-6} inches/inches/hour, where the mean creep rate is determined using a power law model.

21. The method of claim 17 wherein the zircon refractory has a mean creep rate at 1180°C and 1000 psi of less than 3.0×10^{-6} inches/inches/hour, where the mean creep rate is determined using a power law model.

22. The method of claim 17 wherein the zircon refractory has a mean creep rate (MCR) at 1180°C and 250 psi and a 95 percent

confidence band (CB) for said mean creep rate such that the CB to MCR ratio is less than 0.5, said mean creep rate and said 95 percent confidence band being determined using a power law model.

23. The method of claim 17 wherein the zircon refractory has a mean creep rate (MCR) at 1180°C and 1000 psi and a 95 percent confidence band (CB) for said mean creep rate such that the CB to MCR ratio is less than 0.5, said mean creep rate and said 95 percent confidence band being determined using a power law model.