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**An Assessment of Materials for Use
in a Solar Ceramic Receiver
for Chemical Process Heat**

V. J. Tennery
G. W. Weber

OAK RIDGE NATIONAL LABORATORY
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METALS AND CERAMICS DIVISION

AN ASSESSMENT OF MATERIALS FOR USE IN A SOLAR CERAMIC
RECEIVER FOR CHEMICAL PROCESS HEAT

V. J. Tennery and G. W. Weber

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FOREWORD

Under the sponsorship of the Advanced Solar Thermal Technology Branch (M. Gutstein, Chief) of the Solar Thermal Power Program, ORNL has been studying possible applications for high-temperature (above 260°C) solar heat in the manufacture of fuels and chemicals. During the past year, these studies have identified several possible chemicals applications in the 260°C to 1300°C range and several attractive fuels possibilities at temperatures as high as 2200°C.*

In reviewing the solar central receiver designs that might be matched to the various fuels and chemicals processes, it became apparent that only those processes requiring temperatures below 600°C could be served with "current technology," that is, with central receiver designs that might be built in the early 1980s. Considerable design and development effort is going into "advanced" central receiver systems (with peak temperatures less than 1300°C), which can be applied to some of the products we have identified. The "advanced" program does not yet include support for longer range, higher temperature systems that might be needed in several innovative cycles for fuels and fertilizer manufacture.

The materials assessment that follows grew out of ORNL's examination of solar heat applications in the 600 to 1300°C and the 1300 to 2200°C regimes. It suggests certain program needs if these advanced applications are to be pursued as a part of the Advanced Solar Technology Program.

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*S. E. Beall, Jr. and C. E. Bamberger, "Solar Fuels and Chemicals Study, Results," p. 207 in *Proc. Conf. Focus on Solar Technology: A Review of Advanced Solar-Thermal Power Systems*, Nov. 15-17, 1978, Denver, Colorado, CONF-781103, DOE/JPL-1060-78/5.

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AN ASSESSMENT OF MATERIALS FOR USE IN A SOLAR CERAMIC
RECEIVER FOR CHEMICAL PROCESS HEAT

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ABSTRACT

Certain ceramic materials have mechanical properties that make them attractive candidates for structural use in high-temperature solar receivers (heat exchangers) for process heat applications. These process applications would involve chemical reactions between solid and gaseous reactants at temperatures of up to 2200°C. Temperatures above 1000°C are generally considered to be beyond the allowable region for conventional alloys because of their melting points, lack of mechanical strength, and high oxidation rate at these temperatures. Use of refractory ceramic receivers is thus the only viable choice above 1000°C and could conceivably simplify system design requirements even for lower temperature units by minimizing the requirement for over-temperature excursion protection. Candidate ceramic materials were assessed in this work for their potential in meeting the requirements of high-temperature heat exchangers for solar process heat applications.

Candidate ceramic materials were evaluated on the basis of two potential temperature operating regimes: 600 to 1300°C (1100 to 2400°F) and 1300 to 2200°C (2400 to 4000°F). Discussion of properties important to the proposed application includes thermal shock resistance, tensile strength, creep resistance, oxidation resistance, vaporization rate, chemical inertness to process reactants and products, cost, and fabricability. Using these properties for screening purposes, materials most suitable for the two operating regimes were selected.

Many ceramic materials were considered for the 600 to 1300°C operating regime. Many suitable structural ceramics have been fabricated on an industrial scale into extended surface geometries and evaluated in earlier research and development programs. On the basis of a significant data base on tensile strength, thermal expansion, thermal conductivity, fabricability, and stability, the leading candidates were identified, in decreasing order of preference, as (1) silicon carbide, (2) magnesium oxide, (3) cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) known as MAS (4) aluminum oxide, (5) silicon nitride, (6) silicon aluminum oxynitrides ($\text{Si}_x\text{Al}_y\text{N}_z\text{O}_2$) known as sialons, and (7) beryllium oxide.

Selection of candidate materials for the 1300 to 2200°C regime was restricted because of the insufficient property data and operational experience on key performance parameters.

Potential candidates were identified on the basis of existing data and key weaknesses in that data base were identified that would be important in providing more accurate assessment results. Leading candidates were identified, in decreasing order of preference, as (1) zirconium oxide (Y_2O_3 stabilized), (2) magnesium oxide, (3) cerium oxide, (4) beryllium oxide, (5) calcium oxide, and (6) thorium and uranium oxide.

Materials needs identified for the 600 to 1300°C regime include industrial fabrication, economic assessments, and receiver design as well as in-use simulation for silicon carbide, MgO , and MAS. Needs for the 1300 to 2200°C regime include selected bulk property measurements, microstructural and microchemical property determinations, industrial availability assessment, and in-use simulation with scaled-down units for stabilized ZrO_2 and MgO . Development of a usable specification methodology for ceramics was identified as a key area limiting successful implementation of these materials in high-performance applications.

1. MATERIAL PROPERTY CONSIDERATIONS

Certain ceramic materials have mechanical properties that make them candidates for use in high-temperature solar receivers (heat exchangers) for process heat applications. These applications include processes where heat is required for chemical reactions between both gaseous and solid reactants. Currently, the combustion of fossil fuels such as natural gas or oil provides the process heat for these applications. A properly designed heliostat field can have the capability of providing a thermal flux at the receiver surface that could maintain a process temperature as high as 2200°C, depending on the flux value, the receiver design, and the heat transfer processes operative on both sides of the heat exchanger (HX). Such high temperatures are clearly beyond the upper temperature limit of use for all conventional structural alloys. Even for process heat applications requiring temperatures in the range of 1000 to 1400°C, conventional alloys are not acceptable for consideration because of their low melting points, lack of mechanical strength, and high oxidation rates. However, for applications below 1000°C, selected alloys such as certain stainless steels may be considered if the receiver system

design is such that the receiver structure is suitably protected from over-temperature excursions. The use of refractory ceramic receivers is probably the only choice for temperatures above 1000°C, but even for the relatively low-temperature applications ceramics could conceivably simplify system design. Certainly, the requirement for over-temperature excursion protection would be much less critical for ceramic than for alloy units.

In the following discussion, candidate ceramic materials for use as a solar receiver and process heater will be discussed for two potential temperature operating regimes: ~ 1300 and $\sim 2200^\circ\text{C}$ (2400 and 4000°F). The higher application temperature (2200°C max) is such that the number of candidates is small and the data base that currently exists for ceramic materials is very limited. At application temperatures up to 1300°C a larger list of potential candidate materials is available. However, the present state of ceramic HX fabrication technology also restricts this list to a relatively small number of candidates at the present time. Discussion of candidate ceramic materials for both temperature limits will be presented in a following section.

Before discussion of the specific structural ceramic candidates that are to be considered, it will be beneficial to review some of the key properties important to the proposed application. Refractory structural ceramics fail mechanically by brittle fracture because unlike metals, there is negligible plasticity at the tip of cracks, which are produced by stresses applied to the material. This characteristic makes the design of any ceramic structure much more demanding than is the case for metallic structures. For ceramics it is imperative that stress concentrations be minimized under both equilibrium and perceived transient thermal conditions in the unit. The importance of this requirement has clearly been demonstrated in various research and development programs that have examined application of structural ceramics in gas turbine engines and HXs.

The ceramic properties considered to be of the highest importance in the selection of a materials candidate for a solar receiver process

heater involve resistance to chemical attack and brittle fracture. The following properties, except for fabricability, are of importance within the temperature range of intended service, including start-up, shutdown, and excursion conditions:

1. thermal shock resistance (including phase stability),
2. tensile strength or modulus of rupture,
3. creep strength or creep rate,
4. oxidation resistance,
5. vaporization rate,
6. chemical inertness to process reactants and products,
7. fabricability and cost.

Each of the seven listed characteristics is discussed below. Ceramic candidates for the two application temperatures are discussed later.

1.1 Thermal Shock Resistance

The thermal shock resistance of a brittle solid is not a discrete physical property, but in fact consists of a complex combination of the physical properties of the material, the material geometry, and the heat transfer coefficients operative at the material surface in the particular application. The material properties that influence thermal shock resistance are defined and will be discussed briefly. The geometric parameters applicable to actual solar receivers and process heater designs are unclear at present and their identification for candidate designs must be an objective of future work. Similarly, the heat transfer processes and coefficients under anticipated operating conditions is also an objective requiring definition. Thermal shock resistance of the structural elements in a ceramic solar receiver and protection against large-temperature excursions during start-up and cloud passage will be of major importance.

There are five thermal shock parameters that have been identified as applicable to a brittle solid such as the elements considered here. These are conventionally designated by the symbol "R" accompanied by from zero to four prime symbols.¹⁻⁵ The complexity of the stress-material interaction increases in progression from the definition of

R to R'''' . This discussion will focus on the simpler interaction concepts because more extensive experimental verification exists for them and they are considered more applicable to discussion of a real system.

The brittle material with the higher value of these parameters is conceived as more resistant to cracking from thermally-induced stress. Values of the R , R' , and R'' parameters are presently known only for relatively simple shapes. The R''' and R'''' parameters are reportedly measures of the resistance of a brittle solid to microcracking and the accompanying degradation of mechanical strength, but these more complex parameters are not well enough understood for discussion here.

The R parameter is related to the material properties by the relation:

$$R = \frac{S_t(1 - \mu)}{E\alpha}, \quad (1)$$

where

- S_t = fracture tensile strength,
- μ = Poisson's ratio,
- E = Young's Modulus of Elasticity, and
- α = linear thermal expansion coefficient.

This parameter is related to the temperature change in the surrounding medium that will induce thermal fracture (ΔT_f) by:

$$\Delta T_f = R \cdot S, \quad (2)$$

where S is the geometric shape factor appropriate to the R parameter. The R parameter is applicable to a brittle solid under conditions where the surface heat transfer coefficient is essentially infinite.

The R' parameter is generally considered to be more applicable to actual system design in describing the relation between thermal conditions and the resulting stress and is equal to the product of the thermal conductivity of the solid and the R parameter previously described. The maximum thermal flux, $Q_{\max}$, that can be applied to a specific

object of the brittle solid without fracturing is equal to the product of R' and an applicable geometric shape factor, S' . The temperature difference between the object and its surroundings that will just induce fracture is given by:

$$\Delta T_f = R' \cdot S' \cdot 1/h, \quad (3)$$

where h is the surface heat transfer coefficient applicable to the geometric shape under the specified conditions.

Lastly, the R'' parameter is related to the thermal fracture resistance of a brittle shape having an imposed constant rate of change of surface temperature. The surface heat transfer coefficient is allowed to vary in this case. The maximum rate of temperature change that can be imposed without fracture is given by the product of R'' and S'' , the geometric shape factor applicable to the R'' parameters. For example, application of this concept to an infinitely long cylinder of radius r_m gives for the outer surface:

$$(dT/dt)_{\max} = \frac{aS_t(1-\mu)}{E\alpha} \frac{8}{r_m^2}, \quad (4)$$

where

$$\begin{aligned} (dT/dt)_{\max} &= \text{maximum cooling rate that will not induce fracture,} \\ a &= \text{thermal diffusivity of the solid,} \\ S_t &= \kappa/\rho \cdot C_p, \text{ where } \rho = \text{density and } C_p = \text{specific heat,} \\ r_m &= \text{cylinder radius.} \end{aligned}$$

Because ceramic materials are inherently weaker in tension than in compression, Eq. (4) describes the maximum cooling rate that will not induce fracture on the surface of a brittle cylinder, such as an HX element, by the tensile stresses developed during cooling. Similar relations have been derived for a few other simple shapes. More sophisticated methods may be applied to analyze the response of ceramic materials to transient stress fields, but the concepts reviewed here are sufficient for preliminary ceramic material candidate consideration and screening. It is anticipated that these concepts

should be employed early in a solar process heater program to select the structural ceramic candidate or candidates. The material property data base required to evaluate ceramic materials based on these R -type parameters is very limited, particularly in the high-temperature range.

An evaluation of R and R' parameters for some high-performance ceramic materials including various types of silicon carbide, silicon nitride, and mullite has been conducted.⁶ Values for the R parameter at 1000°C (1830°F) ranged from 7.2×10^2 K for hot-pressed silicon nitride to 1.6×10^2 K for sintered α SiC. The thermal stress resistance parameter R' ranged in value from 2.5×10^4 W/m for chemically vapor deposited SiC to 1×10^3 W/m for mullite.

1.2 Tensile Strength

Brittle solids are inherently weaker in tension than in compression because of lack of plasticity at crack tips as noted previously. Therefore, they are also very sensitive to relatively small flaws such as pores or other characteristic fabrication defects. The measured tensile strengths or the more conventional moduli of rupture for structural ceramics are very dependent not only on the actual strength value for the material, but also on the test procedure, etc. Strength data for structural ceramics at temperatures much above 1400°C are, in general, lacking. It is obvious from the previous section that the tensile fracture strength is a key property in the expressions for thermal shock resistance and this data base would have to be developed for selected ceramic candidates at appropriate temperatures in order to make a refined material selection.

1.3 Creep Strength

At sufficiently high temperatures, even the more refractory ceramic materials will exhibit measurable creep at modest stresses. This creep is normally a combination of creep due to grain boundary phases and creep deformation of the refractory major phase or phases. The former type of creep is more common in many conventional applications

of ceramics because the less refractory grain boundary phases are employed to facilitate fabrication. Careful attention to the relation between secondary grain boundary phase composition and content and creep properties will be most important in evaluating materials for use in the 1300 to 2200°C regime. The data base of creep properties for ceramic materials in this temperature range is very sparse at this time.

Although the data base for creep of ceramics at temperatures below 2200°C is somewhat more extensive, there is considerable variability between samples of the same ceramic material and difficulty in defining the relation between the creep value and microstructural features. For these reasons, definitive creep studies of simple oxides and more complex refractories have not yet been conducted. From the data that have been obtained, it appears that differences among different materials are generally unrelated to intrinsic properties such as compositional or crystal structure variations but are more related to extrinsic characteristics such as microstructural features including grain size, porosity, and the amount and type of amorphous grain boundary phase present. Most refractory oxides rapidly decrease in strength and rigidity above 1000°C and develop significant plasticity above 1300°C but are markedly superior to metal alloys in this temperature regime.⁷ For example, at 1100°C Inconel has a creep rate under a 100-psi stress⁸ comparable to that experienced by magnesia under a 1200-psi stress.⁷ Furthermore, alumina, zirconia, and silicon carbide are significantly more resistant to creep than is magnesia.

1.4 Oxidation Resistance

Unless acceptable transparent receiver "windows" are available, the receiver surface facing the heliostat field will obviously be in an air environment, while the surface on the secondary side may or may not be in a high oxygen potential, depending on the chemical reaction being conducted in the process heater. It is clear that for both temperature regimes, oxidation resistance will be essential in order to provide a reasonable operating lifetime. In the ~1300°C regime,

nonoxide ceramics may be considered because some attain an oxidative protective film that greatly reduces the effective oxidation rate. In addition to oxides, such structural ceramics as silicon carbide, silicon nitride, or the newer sialons appear to be reasonable candidate materials because they can form amorphous oxidation protective films. The ability of these films to maintain their protective integrity during multiple heating and cooling cycles anticipated in an operating solar receiver or process HX should be an important material consideration in any future solar process heater development programs. In the 1300 to 2200°C range, only selected oxides are considered sufficiently stable because the refractory oxides such as MgO or stabilized ZrO₂ are in their highest oxidation states and will therefore undergo no further oxidation.

1.5 Vaporization Rate

Mass loss from the ceramic surfaces in an HX due to an appreciable vapor pressure of various gaseous species over the ceramic is considered to be a major concern, particularly for the 1300 to 2200°C regime. In the below 1300°C regime, this is presently considered to be of relatively minor concern. The data base for vaporization rates from free surfaces of MgO, stabilized ZrO₂, HfO₂, ThO₂, UO₂, BeO, and CaO is relatively sparse at present. It is obvious that selective vaporization from the ceramic material would be unacceptable. For example, loss of the stabilizing oxide from a ZrO₂ ceramic at a rate that would destabilize the ZrO₂ within the anticipated operating lifetime of the process heater would be unacceptable. Some experimental screening studies of vaporization rates from a limited number of candidate materials will be required as an early part of a high-temperature solar process heater program.

1.6 Chemical Inertness

On the secondary side of the receiver, assuming that a fixed-boundary heat exchanger design is employed, there must be minimal

reaction between the ceramic partition and the process reactants or products. It is anticipated that as a first approximation, candidate ceramic materials can be evaluated from this point of view by means of conventional high-temperature thermodynamic calculations followed by screening tests to determine if the kinetics of the calculated reactions are sufficient to degrade the material during the design lifetime.

1.7 Fabricability

Ceramic materials presently considered to be viable candidates for use in solar receivers and process heaters can currently be fabricated by a limited number of procedures. Present fabrication limitations and the current status of joining technology for ceramics restrict the geometries realistically available for consideration in the near term.

Ceramic materials are fabricable in geometries appropriate to conventional HX elements such as smooth tubes, finned tubes, and plates. Recent technological advances have been made in fabrication of ceramic structures of "extended surface geometries." An example is the honeycomb, which has been extensively tested for use in advanced heat engine air preheater wheels and as catalyst supports for automotive applications. These extended surface geometries offer the potential for the design of relatively compact HXs, compared to more conventional tube and manifold-type designs. For an HX application such as considered here, it will be quite important that leakage between the primary and secondary sides of the HX be minimal if a fixed boundary design is employed. This consideration will be most important if the pressure on the process side is to be maintained significantly above or below atmospheric pressure. This condition will require a high degree of mechanical integrity for the surface across which the principal heat transfer occurs as well as for all joints used to seal the elements to the inlet and outlet ducts. Joining systems for use below 1300°C can take many forms, depending on the load-bearing situation, temperature, and base materials. Joining can normally be accomplished either by machining pieces to fit or by placing a sealing material between the two pieces. The machining of brittle materials to close tolerances is an expensive

and difficult process requiring a precise match of transient thermal properties to minimize mechanical loading in a direct mechanical joint. Therefore, this approach is not normally considered as a viable method of joining. Sealing can also be accomplished by using some flexible or yielding (compliant) material at the design operating temperature, such as high-temperature fibrous ceramic insulation or a yielding glass, which will compensate for thermal expansion mismatches. Development of solid state as well as the more common viscous brazes for ceramic materials is an alternate approach. Solid state brazes developed for nonoxide materials such as Si_3N_4 and SiC have demonstrated high toughness and reasonable strength.⁹⁻¹¹ Brazing allows a continuous bond that avoids the stress concentrations of mechanical attachment and the concern for long-term stability of compliant layers. The present data base for stable joining systems for refractory structural ceramic oxides for potential use in the $\sim 2200^\circ\text{C}$ regime is extremely sparse and should have a major focus in any program for fixed-boundary HX designs. If a regenerative wheel HX design is also considered, facing and rim seal systems, thermally induced distortions, and the required shaft bearings should receive major attention. Conventional ceramic fabrication technology may be adequate for preparation of prototypical ceramic HX elements, depending on the features of the design. Demonstration of this ceramic fabrication capability on at least a limited industrial scale should be a specific objective of any future program on materials research and development for solar process heater applications.

2. CANDIDATE MATERIALS FOR THE 600 TO 1300°C (1100 TO 2400°F) REGIME

A considerable number of structural ceramic materials may be considered for use below 1300°C. Several of these materials have been industrially fabricated in the form of extended surface structures and evaluated in earlier research and development programs in the United States. Other ceramic formulations have the potential for being fabricated into this type of structure but have not been previously pursued because of lack of a clear need. In this section, the ceramic materials

that have been fabricated both in extended surface geometry and more conventional geometries (such as smooth or finned tubes) and that are considered to be good candidates at this time for receiver application will be discussed. Tennery and Wei¹² recently published the results of a national assessment of the status of materials technology for both ceramic and metallic HXs for use as waste heat recovery recuperators. Conclusions from that assessment pertaining to structural ceramic materials are reasonably applicable to the present potential solar application, and a brief review of those results will be helpful. One distinction between a more conventional recuperative HX application and a solar process heater is that in most industrial recuperator applications, the furnaces are more or less continuously in operation and the recuperator experiences relatively few heat-up and cool-down cycles during its service life; while in a solar application, such cycles will be frequent, at least daily. Consequently, the thermal shock resistance of a solar process heater is considered to be very important when considering use of ceramic materials. From the previous discussion of the expressions describing thermal shock parameters, those materials having the lowest elastic modulus and thermal expansion coefficient will tend to be most resistant to fracture due to thermal transients. Similarly, those materials having the highest values of tensile strength, thermal conductivity, thermal diffusivity, and Poisson's ratio will also have better thermal shock resistance. Most refractory structural ceramics have similar values for Poisson's ratio or elastic modulus, and thus the properties that tend to be most useful from a selection standpoint are the thermal transport properties, the tensile strength, and the thermal expansion coefficient. A reasonable range of expansion ratio values of ~ 21 is observed at 1000°C for relatively refractory ceramics.¹³ Tensile strengths typically have a ratio range of up to ~ 15 at 1300°C,¹⁴ while thermal conductivities may have a ratio range of ~ 7 at temperatures of about 1400°C.¹⁵ The leading candidates for consideration on this basis include cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) often referred to as MAS, spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) based ceramics (LAS), modified spodumene ceramics (AS), silicon nitride, silicon aluminum oxynitrides (sialons),

beryllium oxide, magnesium oxide, silicon carbide, and alumina. The appropriate information on these materials for this temperature range will be summarized below to permit evaluation of their potential for this application.

Magnesium oxide has a high melting point (2800°C), is very stable in oxidizing atmospheres, and is stable in reducing atmospheres to temperatures well above 1300°C.¹⁶ However, magnesia also has a high thermal expansion coefficient ($13.5 \times 10^{-6}/^{\circ}\text{C}$ from 0 to 1000°C),¹⁷ a relatively low thermal conductivity [6.7 W/m (0.016 cal/s cm °C) at 1000°C],¹⁵ and a tensile strength of approximately 12,000 psi at 1000°C,¹⁴ which result in a relatively poor thermal shock resistance. Fabrication technology is well established by most techniques for MgO.

Beryllium oxide is another ceramic material with some desirable properties, notably good thermal shock resistance, for application as a ceramic HX material. Although the coefficient of thermal expansion and room temperature tensile strength of BeO are comparable to Al_2O_3 , its thermal conductivity at 1200°C is up to four times higher than that of Al_2O_3 ,¹⁵ thus giving BeO significantly better thermal shock resistance. However, the rapid decrease in tensile strengths above 1100°C¹⁸ found in some studies of BeO and the significant restraints placed on manufacturing operations of this material because of the reported toxicity of fine beryllia powder make it less attractive for consideration as a serious candidate material. Some consideration would need to be given, as well, to mechanisms for potential "in-use" release of small particulates of BeO to the environment if this ceramic material is considered to be a serious candidate.

Aluminum oxide is one of the most chemically stable and mechanically strong oxides at moderate temperatures. Its thermal expansion coefficient is comparable to beryllia in this temperature regime¹⁷ and its thermal conductivity¹⁵ is comparable to magnesia. Room temperature tensile strength is about twice that of magnesia.¹⁸ At lower temperatures alumina has very high rigidity, equalled only by beryllia. Above 1000°C, however, alumina ceramics lose strength fairly rapidly, depending on their secondary phase compositions; by 1300°C the tensile

strength has decreased to one-sixth of its room temperature value,¹⁸ while the strength of MgO has decreased only by one-half.¹⁴ Fabrication technology for alumina ceramics is well established for many manufacturing techniques.

The MAS, LAS, and AS ceramics have exceptionally low thermal expansion coefficients ranging from 1/27 (for LAS) to 1/4 (for MAS) of the magnesium oxide values in the same temperature regime. Flexural strength of MAS is about one-half that of alumina at 1150°C.¹⁹ Because of the low thermal expansion and moderate strength, these materials have exceptionally good thermal shock resistance. However, because of the relatively low melting point or dissociation temperature of some of the eutectic systems ($\approx 1450^\circ\text{C}$ for MAS),²⁰ the maximum use temperature of even the highest melting point materials in this class (MAS) would be 1300°C or less. Unfortunately, MAS also has the highest thermal expansion coefficient of these three ceramic materials.

Silicon carbide, because of its high melting point and low vapor pressure, has exceptional stability in vacuum and inert atmospheres to temperatures above 2000°C. In oxidizing atmospheres, a vitreous SiO_2 film forms and provides excellent protection to 1500°C.²¹ Above 1200°C this film is converted to cristobalite after an induction period, and the rate of oxidation attack increases only slightly.²² Although physical properties vary dramatically with fabrication technique and the specific phase content and microstructure, flexural strengths at 1000°C are up to 2 1/2 times that available from the best state-of-the-art oxide materials and show little degradation to 1300°C.²³ The high thermal conductivity (2 to 5 times that of Al_2O_3 at 1000°C),²⁴ low thermal expansion (approximately half that of Al_2O_3),²⁵ and high tensile strength at temperatures above $\sim 1000^\circ\text{C}$ result in excellent thermal shock resistance. The broad range and current industrial expertise in fabrication processes for SiC ceramics make this material a leading contender for potential application in a solar process heat receiver for process temperatures up to 1300°C.

Silicon nitride and the sialons have excellent high-temperature strength and thermal shock resistance and good stability in an oxidizing environment to 1000°C. Hot-pressed silicon nitride has a tensile

strength four times that of siliconized silicon carbide at 1000°C with a thermal expansion coefficient one-sixth that of MgO and 25% less than SiC.²⁶ Hot pressed Si_3N_4 at 1100°C has only one-fourth the thermal conductivity of SiC,²⁷ so that thermal shock sensitivity and heat transport properties may make it less desirable than SiC for potential application in a solar receiver. The difficulty of fabricating large and/or intricate shapes of Si_3N_4 with the properties of hot-pressed material has led to the development of reaction bonded material that has somewhat less desirable properties for structural applications. The tensile strength of reaction bonded material at 1000°C is less than half that of the hot-pressed variety.²⁶ Recent results²⁸ on commercially available hot-pressed silicon nitride have also shown a 50% or greater decrease in strength on oxidation at 1000 to 1400°C due to surface pitting. This phenomenon is the source of much current investigation into hot-pressing additives,²⁹ but the current state-of-the-art is such that silicon nitride has less appeal for solar receiver applications than does silicon carbide or some of the oxides.

New ceramic materials based on mixtures of zirconia and mullite have also been reported recently and may have applicability for use in HX elements in this temperature regime.

Based on these considerations and the limited data presently available, a qualitative priority list is provided in Table 1 for refractory structural ceramics for evaluation in the ~1300°C temperature regime for use in a solar receiver or process heater.

Table 1. Priority List for Refractory Structural Ceramics for Use in HXs up to ~1300°C

Priority	Ceramic Material
1 (highest)	Silicon carbide
2	MgO
3	MAS
4	Al_2O_3
5	Silicon nitride
6	SIALONS
7 (lowest)	BeO

3. CANDIDATE MATERIALS FOR THE 1300 TO 2200°C (2400 TO 4000°F) REGIME

Evaluations of candidate materials for the higher temperature regime is more difficult because of a relative lack of sufficient ceramic materials data or operational experience on key performance parameters. This survey will, therefore, point out both potential candidates from existing data and weaknesses in the data base, which would require additions before a more accurate assessment and material selection process is possible.

Consideration is limited to only a few materials, all of which are oxides with adequately high melting points. Although many non-oxides possess sufficiently high melting points and possibly attractive physical properties in this temperature regime, the requirement of an oxidizing atmosphere for the solar receiver process heater makes this restriction essential in our view. On the basis of our arbitrary criterion of operating the material at no more than 90% of the melting point, the choices of available oxide materials with melting points above 2475°C is sharply reduced to include MgO, CaO, ZrO₂, HfO₂, BeO, ThO₂, UO₂, and CeO₂. The available information on these materials in evaluating their potential for application in a very high-temperature solar receiver for this temperature regime is summarized below. Applicable properties are listed at the highest temperatures at which measurements have been published as a basis for identifying data inadequacies.

Magnesia has an adequately high melting point (2825°C) but is restricted somewhat for high thermal transient stress applications by its relatively high coefficient of thermal expansion ($12.6 \times 10^{-6}/K$ from 1000 to 2000°C).³⁰ This disadvantage is partially offset by a relatively low thermal conductivity of 14 W/m °C at 2000°C.³¹ The actual value of tensile strength at temperatures above 1350°C is unknown as a function of microstructure and purity, but as strength drops rapidly to 10 to 40% of its room temperature value up to 1350°C, this ceramic material will certainly have very low tensile strength at 2200°C. Measurements of vaporization and volatilization rate indicate that significant vaporization of magnesia can be expected in the

range 1600 to 1900°C in vacuum,¹⁶ and these results may indicate potential difficulty at 2200°C in an oxidizing atmosphere.

Magnesia has, however, been used in the "Wisconsin Process" pebble furnace for fixing atmospheric nitrogen at temperatures to 2200°C.³² That experience demonstrated that 90% MgO ceramics have the ability to function at these temperatures for nitrogen fixation. The circulating pebbles in the bed suffered a reported 5% breakage at 2200°C with estimates of less than 3% breakage at 2000°C, but the magnesia roof refractories showed no secondary spallation in one year of operation and were estimated to be able to survive an additional four to five years of operation at shutdown even with a long suspended arch roof in the furnace. This experience would indicate a significant potential for use of magnesia in a very high-temperature ceramic solar process heater, but the result also indicates a need for relevant property measurements from 1300 to 2200°C to validate serious consideration of this material.

Calcium ceramics (CaO) are potentially low in cost and very refractory, but in contact with water a rapid reaction occurs to form a hydroxide. Ceramic bodies made of calcia will hydrate in air and typically decompose in a few days. Material with very high densities can be kept only a few hundred hours in relatively dry atmospheres before failure due to hydration. Despite significant attempts at stabilization techniques, this characteristic is felt at this time to essentially rule out calcia from further consideration. Otherwise, the properties of calcia ceramics are similar to, but slightly less attractive than magnesia.

Ceramics based on ceria, CeO_2 , are characterized by poor thermal shock resistance because of low thermal conductivity (approximately one-eighth that of MgO at 1600°C)³³ and a high coefficient of thermal expansion (approximately equal to MgO at 1600°C).³⁴ Significantly, although ceria is stable in air, it may be reduced to Ce_2O_3 with a melting point of 1690°C if heated in an atmosphere with a relatively low oxygen potential.³⁵ Although it is more abundant than zinc, cerium is relatively expensive. Because of these considerations as well as

the lack of high-temperature data for ceria ceramics, ceria would be a less attractive candidate than other oxides such as MgO.

Beryllia, BeO , as previously described, has excellent thermal shock resistance, very high thermal conductivity, and is relatively weak in tension at 1300°C . However, in compression at 1600°C , it is one of the strongest oxides known.³⁶ It is also readily volatilized due to reaction with water vapor at temperatures above 1650°C . Ceramic bodies heated in gas-fired furnace atmospheres have, for example, experienced considerable weight loss.^{37,38} Because of these considerations, as well as the previously mentioned toxicity concerns for beryllium, we feel that a beryllia ceramic is a less desirable candidate for potential solar receiver applications.

Thoria, ThO_2 , has a very low vapor pressure at high temperatures, the highest reported melting point of all oxides, and is the most resistant to attack by most metals. However, thoria ceramics have relatively poor thermal shock resistance because of the low thermal conductivity (one-sixth that of MgO at 2000°C).³⁹ It also is significantly radioactive due to its radon decay products that are released at temperatures approaching 2000°C . It would, therefore, be an unlikely candidate for this application.

Uranium dioxide, UO_2 , is readily oxidized to U_3O_8 which, in turn, above 750°C is decomposed to a lower oxide.³⁵ This oxidation sequence is quite destructive to urania ceramics. Thermal conductivity of UO_2 is one-sixth that of MgO at 2000°C with a comparable thermal expansion coefficient,³⁹ so the thermal shock resistance of urania ceramics is generally low. Uranium dioxide is slightly radioactive, which would also make it much less desirable for consideration than other ceramics.

Zirconia (ZrO_2) and hafnia (HfO_2) have similar properties including exceptionally low thermal conductivity (one-third that of MgO at 1400°C), a high coefficient of thermal expansion (40% greater than MgO to 2000°C),^{39,40} and catastrophic volume changes accompanying polymorphic phase transformations at $\sim 1000^\circ\text{C}$ so that stabilization via phase compositional modifications is required. Stabilization can be achieved by solid solution in the host oxide of CaO , MgO , Y_2O_3 , or Tm_2O_3 , which result in high but uniform thermal expansions.³⁵ Overall,

thermal shock resistance would still be relatively low compared to that of some other candidate oxides. Zirconia and hafnia are both characterized by relatively high stability and chemical inertness at high temperatures. Hafnia would normally be preferable for most refractory applications but is significantly more expensive. Zirconia has a relatively high tensile strength and resistance to creep at high temperature (approximately twice that of MgO at 1300°C)¹⁴ and does not display appreciable volatility in vacuum below 2300°C, which is ~700°C higher than a recommended use temperature for MgO.⁴¹ The possible selective volatility of the stabilizing additive is a potential concern and would require study to ensure that the phase stability of these ceramics would be adequate for long time periods at high temperatures. Despite its relatively low thermal shock resistance and low thermal conductivity, stabilized zirconia should be a material for serious consideration for high-temperature solar process heaters because of its refractoriness, high-temperature strength, and stability.

A qualitative ranking of these ceramic materials for potential use in a very high-temperature solar process heater in the 1300 to 2200°C regime is given in Table 2.

Table 2. Priority List for Ceramic Materials
in a Very High-Temperature Solar Process
Heater in the 1300 to 2200°C Regime

Priority	Ceramic Material
1 (highest)	ZrO ₂ (Y ₂ O ₃ stabilized)
2	MgO
3	CeO ₂
4	BeO
5	CaO
6 (lowest)	ThO ₂ /UO ₂

4. MATERIAL NEEDS

The preceding sections serve to identify some of the key factors considered to have first level importance in dictating the selection of candidate ceramic materials for potential solar process heater

application. Table 3 summarizes the pertinent information for the leading candidates for the two temperature regimes. For the lower temperature regime [i.e., up to 1300°C (2400°F)], the results obtained in the Black and Veatch (B&V)⁴² and Sanders Associates⁴³ ceramic solar receiver programs funded by EPRI and DOE are very significant in providing a baseline for our purposes here. The B&V design employs a siliconized silicon carbide vertical tubular geometry and mechanical compression joints on both upper and lower headers. The design for this unit has the objective of providing air at temperatures to 1200°C (2200°F) to run an open cycle turbine to produce electricity. The particular type of silicon carbide employed and the present joint design are felt to be usable up to about 1288°C (2350°F).⁴⁴ This form of silicon carbide probably is usable up to about 100°C below the melting point of silicon (1420°C) because silicon is a major secondary phase in this material. The work of Sanders Associates pertaining to a ceramic solar receiver also included silicon carbide in honeycomb form with the objective of producing high-temperature air at about 1093°C (2000°F) for use in generating electric power. Because of the encouraging results in these and other programs, we have identified ceramic silicon carbide as having the highest priority for potential application up to 1300°C for solar chemical process receivers. MgO, MAS, Al₂O₃, and silicon nitride ceramics are considered to have priorities 2 through 5, respectively. It is strongly recommended that candidate ceramics at least through priority 5 be included in a materials evaluation program for the 1315°C regime. Such a program would consider selected property studies plus industrial fabrication and economic assessments based on early receiver conceptual designs. Tests of HX elements made of materials through priority 3 should be conducted under conditions expected in the receiver.

For the temperature regime of 1300 to 2200°C, the data base for candidate ceramic materials for use in a solar receiver is, as indicated in Sect. 3, very sparse. Based on property data available at this time, we have ranked candidate ceramic materials by priority with stabilized ZrO₂, MgO, CeO₂, and BeO ceramics having priorities 1 through 4, respectively. It is strongly recommended that stabilized

Table 3. Ceramics for Use in Solar Chemical Process Receivers

Material	Thermal Expansion Coefficient	Tensile Strength	Thermal Conductivity	Comments
<u>600-1300°C Application</u>				
Beryllium Oxide	Medium	Medium	High	Toxicity problem; strength decreases rapidly >1000°C
Magnesium Oxide	High	Medium	Low	Good stability; poor thermal shock resistance
Aluminum Oxide	Medium	Medium	Low	Strength decreases rapidly >1000°C
Cordierite (MAS)	Low	Medium	Low	Low eutectic melting points
Spodumene (LAS)	Very Low	Low	Low	Low eutectic melting points
Silicon Carbide	Low	High	Very High	Much fabrication expertise available
Silicon Nitride	Low	Very High	Medium	Degrades in air at 1000-1400°C
<u>1300-2200°C Application</u>				
Magnesium Oxide	High	Low	Medium	Volatility a problem at higher temperatures
Beryllium Oxide	Medium	Low	High	Toxicity problem
Calcium Oxide	High	Low	Medium	Severe hydration problems
Zirconium Oxide (Stab.) Hafnium Oxide	High	Medium	Low	Requires stabilization; good stability
Cerium Oxide	High	Unknown	Low	Relatively easy to reduce
Thorium/Uranium Oxide	High	Low	Low	Potential radioactivity problems

zirconia and magnesia ceramics be vigorously evaluated at the onset of any solar process heater program with a lower level of assessment work being conducted on ceramic CeO_2 and BeO at the same time. It is anticipated that this early evaluation work on CeO_2 and BeO would be completed relatively early in a program and these materials would then be considered as backup alternatives to the prime zirconia- and magnesia-based ceramic candidates. Work on zirconia- and magnesia-based ceramics for application in very high-temperature solar receivers should include (1) selected property measurements; (2) identification of the microstructural and microchemical properties of these ceramics, which may limit their usefulness in this temperature regime; (3) an industrial availability assessment based on ceramic geometries appropriate to the receiver conceptual designs; (4) testing of scaled-down ceramic HX units using solar or other heat sources under appropriate temperature and other conditions.

A clear need identified during this assessment was the lack of a usable specification methodology for structural ceramic materials. The potential for refractory structural ceramics to perform adequately in advanced energy conversion systems has been limited in the past by generally unpredictable mechanical properties. This general characteristic of these materials results from a poor understanding of the relationship between mechanical and thermal properties and the composition, microstructure, and fabrication history of the brittle ceramics. The considerable sensitivity of the mechanical properties of ceramic materials to microflaws, microstructure, and the grain boundary structure and composition makes it essential that effort be initiated to develop specification sets that analytically relate critical properties to the synthesis, fabrication, and machining parameters employed to make ceramic components. The lack of such a specification methodology and thus the lack of adequate specifications for specific candidate structural ceramics has in the past resulted in unexpected variable high-temperature properties. As a result, the question as to whether various ceramics can be eventually improved so as to ultimately be considered true engineering materials is certainly valid at this time. The development and demonstration of explicit

specifications for selected structural ceramics is an important area that should be addressed in programs of which the objective is to employ or evaluate structural ceramics in solar process heaters.

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