Mechanical Properties of Vacuum-Sintered Equimolar CaO-Y₂O₃ System*

A. S. Wagh,[†] P. S. Maiya, R. B. Poeppel, R. Russell,
T. Suratwala, and D. Roberts

Materials and Components Technology Division
Argonne National Laboratory
Argonne, IL 60439

April 1991

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

4/30/91

DRA

*Work was supported by the U.S. Department of Energy, Nuclear Energy Research and Development Program, under Contract W-31-109-Eng-38.

[†]Also at the Materials Laboratory, Physics Department, University of the West Indies, Kingston, Jamaica.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Mechanical Properties of Vacuum-Sintered Equimolar CaO-Y₂O₃ System

A. S. Wagh,[†] P. S. Maiya, R. B. Poeppel, R. Russell,
T. Suratwala, and D. Roberts

Materials and Components Technology Division
Argonne National Laboratory
Argonne, IL 60439

Oxides of calcium and yttrium (CaO and Y₂O₃) are two of the most thermodynamically stable oxides among those used in ceramic fabrication. The free energies of formation¹ of CaO and Y₂O₃ at 1000 K are -538 and -531 kJ/g-atom, respectively. Thus, they are potential candidate raw materials for container applications in pyrochemical reactions. In addition, a lightweight ceramic material of these oxides or of their composites is preferred to heavy refractory metals for pyrochemical container applications. Despite these attractive properties, no information is available on ceramics of the CaO-Y₂O₃ system in the literature. The purpose of this preliminary study is to fabricate such a composite ceramic material and explore its mechanical properties.

The existence of two phases, viz., CaY₂O₄ and Ca₃Y₂O₆, has been reported by a few investigators. Barry and Roy² described the first synthesis of CaY₂O₄ in powder form. Lopato et al.^{3,4}, studied the phase diagram of the CaO-Y₂O₃ system, in which they also reported the existence of Ca₃Y₂O₆. Both Barry and Roy,² and Lopato et al.,³ prepared the starter powders by dissolving calcium carbonate and yttrium oxide in nitric acid and rapidly evaporating the solution. They sintered the mixtures at 1840°C in air for 3 h to form the compound. The present work describes the fabrication of dense

ceramic material aimed at container applications by vacuum-sintering a mixture of equimolar proportion of CaO and Y_2O_3 . This study also characterizes the mechanical properties, such as flexural strength, fracture toughness and resistance to thermal shock of the composite. The present attempt is a part of a wider study to identify the mechanical and thermal shock behavior of materials most suitable for container applications at high temperatures in aggressive corrosive environments.

FABRICATION OF SPECIMENS

The starter powder was prepared by mixing Ca(OH)_2 and Y_2O_3 powders. The powders were supplied by Mallinckrodt, Inc. and Molycorp Louviers Company, respectively. Both compounds were commercial, chemical grade products. Ca(OH)_2 contained less than 2% of magnesium and other alkali salts such as sulfates. The powders were processed in water containing 6 wt.% of polyethylene glycol binder. The composition was chosen such that the processed powder has approximately the stoichiometric composition of $\text{CaO} \cdot \text{Y}_2\text{O}_3$. The mixture was ball milled for 16 h in alumina milling media. The particle size of the mixed powder ranged from 0.17 μm to 30 μm with a median at 6 μm .

Rectangular bars of dimensions 33 mm x 5.8 mm x 3.6 mm were pressed in a uniaxial mode, perpendicular to the surface of 33 mm x 3.6 mm with a pressure of 42 MPa, and were bisque fired at 800° C for one hour. They were vacuum-sintered for one hour at 1500° C, which was close to the sintering temperature of CaO . Based on literature data, sintering at 1500° C is expected to produce a composite rather than a compound.^{4,5} The

pressure during sintering was $\approx 1.3 \times 10^{-4}$ Pa. The furnace was then allowed to cool to the room temperature before the bars were taken out.

PHYSICAL PROPERTIES AND THE MICROSTRUCTURE

The bars were light blue in color. The average bulk density of the bars by direct measurement was 4.17 g/cm^3 , which was 92.3 % of the theoretical density of 4.52 g/cm^3 of the equimolar mixture of CaO and Y_2O_3 . The porosity of ~8% appears to be too high for a container ceramic material. However, detailed investigations by water intrusion in open pores by boiling the specimens in distilled water yielded only 0.36% open porosity, implying most of the pores were isolated closed pores. This conclusion was further supported by the observation that small crucibles made of this material, neither leaked nor wetted, when filled with distilled water.

To explore the structure of this material, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were used. SEM and EDX studies were done on fracture surfaces of the samples. Figure 1 shows a typical SEM micrograph of a fractured sample. Grain structures and grain boundaries are not distinct. Both yttria and calcium oxide are glass-forming materials, and it is likely that a glassy phase may also exist in the composite. However, it was not possible to confirm the existence of a glassy phase by X-ray diffraction studies. The spatial variation in the ratio of Ca and Y distribution, as determined by EDX studies, confirmed that the ceramic product is more of a composite than a uniform compound.

MECHANICAL PROPERTIES

The Young's modulus (E), the shear modulus (G) and the Poisson ratio (ν) were measured by an ultrasonic method.⁶ No appreciable scattering of sound waves by the closed pores was observed during the measurements. Diamond microindentation technique⁷ was used to measure the fracture toughness (K_{IC}), while the flexural strength (σ_f) was measured in a four point bending mode using an Instron machine.

The results are presented in Table 1. The flexural strength of 116 MPa is about 50% higher than that of vacuum-sintered yttria.⁸ This value is lower than the flexural strength of only aluminum nitride amongst the ceramics of low free energies of formation studied by Gogotsi.⁹ The fracture toughness of $2.86 \pm 0.28 \text{ MPa}\sqrt{\text{m}}$ however is about twice that of vacuum-sintered yttria. Young's modulus (~212 GPa) is about 33% higher than that of yttria. Thus the composite has superior mechanical properties as compared to those of yttria ceramics.

The specific fracture surface energy γ ¹⁰ was calculated by using the equation,

$$\gamma = \frac{K_{IC}^2}{2E}, \quad (1)$$

which yielded a value of ~19.2 Joules/m². This is more than twice the value of γ obtained for yttria ceramics.⁸ A closer examination of the scanning electron micrographs of the fracture surfaces (Fig. 1) shows evidence of fracture at the grain boundaries and also through the glassy phase; the former is evident in the tetrahedral grain surfaces, while the latter may be seen by the existence of smoother, nondistinct surfaces.

The critical flaw-size (c) was estimated from the Griffith relation,¹¹

$$\sigma = \frac{K_{Ic}}{1.35\sqrt{c}}$$

Using the values of σ_f and K_{Ic} from Table 1, the critical flaw-size is found to be $\sim 329 \mu\text{m}$. This high value suggests that the composite material can sustain significantly longer flaw lengths prior to failure than Y_2O_3 ceramics.

Table I. Physical and mechanical properties of vacuum-sintered $\text{CaO-Y}_2\text{O}_3$ composite

Property	Measured value $\pm$ standard deviation
Bulk density	4.17 ± 0.04 g/cc (92.3% theoretical)
Open porosity	0.36%
Flexural strength	117 ± 21 MPa
Fracture toughness	2.86 ± 0.28 MPa $\sqrt{\text{m}}$
Young's modulus	217 ± 9 GPa
Shear modulus	87 ± 3 GPa
Poisson ratio	0.25 ± 0.01

THERMAL SHOCK RESISTANCE

To study the thermal shock behavior of the material, the specimen bars were heated in an air furnace for half an hour at the desired temperature. The bars were then quenched in water at room temperature. They were removed from water, dried, and the flexural strength was determined.

Figure 2 shows the flexural strength of the material as a function of the quenching temperature difference (ΔT). The overall thermal shock behavior is very similar to that of yttria⁸ and other ceramics of thermodynamically

stable materials.⁹ A significant deterioration in the flexural strength of the material from 117 to 40 MPa occurred over a narrow range of $\Delta T \approx 177 - 202$ K. For $\Delta T > 202$ K, the degradation is gradual, which is typical of other thermodynamically stable ceramics.⁹ However, the composite material of this study exhibits improved retention of the flexural strength after thermal shock treatment. For example, the room temperature flexural strength of the composite is comparable to that of Sc_2O_3 , which is also a thermodynamically stable at high temperatures.⁹ For ΔT beyond 300 K, the composite material shows a strength (40 MPa), which is twice the value of the strength of Sc_2O_3 (~20 MPa). This retained strength of 40 MPa for the composite is comparable to that of aluminum nitride,⁹ although the latter has a much superior value of room temperature flexural strength (~215-MPa).

A comparison of the thermal shock behavior of the composite and other common materials can be made by means of a thermal shock resistance parameter R''' proposed by Hasselman,¹² which is given by

$$R''' = \frac{E\gamma}{\sigma_f^2(1-\nu)}, \quad (3)$$

Using the data presented in Table 1, the value for the composite is calculated. We compare this value with R''' for two materials which have one of the worst and the best thermal shock behavior. Hasselman has compiled data for porcelain, and alumina reinforced with molybdenum fibres, as the examples of these two extreme cases. When R''' is calculated by using his data, we obtain 2.9×10^{-5} m for porcelain with very poor thermal shock resistance, and 2.4 m for reinforced alumina with excellent

thermal shock resistance. The value for the composite is 4×10^{-4} m, which is closer to the value estimated for the material with poor thermal shock resistance. The poor thermal shock behavior of the composite suggested by the low value of R''' is consistent with the existence of a glassy phase in the material. The improved mechanical properties and the retention of the flexural strength of the composite over that of yttria ceramics following thermal shock suggest an advantage of the composite over single oxide ceramics for container materials. Currently efforts are being made to develop ceramics with other compositions to improve thermal-shock behavior and to achieve optimal mechanical properties of container materials for applications in pyrochemical processes.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Nuclear Energy Research and Development Program, under Contract W-31-109-Eng-38. A. S. Wagh is also at the Materials Laboratory, Physics Department, University of the West Indies, Kingston, Jamaica.

REFERENCES

1. "Thermodynamic Properties of Elements and Oxides", Report # PB83-17405, U. S. Bureau of Mines, Albany, OR (1983)
2. T. L. Barry and R. Roy, "New Rare Earth-Alkaline Earth Oxide Compounds", J. Inorg. Nucl. Chem., **29**, 1243-1248 (1967).

3. L.M. Lopato, A. E. Kushchevskii and A. V. Shevchenko, Dokl. Akad. Nauk UkrSSR, **3B**, 246(1971).
4. L. M. Lopato, G. I. Gerasimyuk, A. V. Shevchenko and S. G. Tresvyatskii, "Phase Equilibria in the Systems Dy_2O_3 - CaO, Y_2O_3 - CaO, Yb_2O_3 - CaO.", Translated from Izvestiya Akademii Nauk SSSR, Neorganicheskie materialy, **9** [3], 427-431 (1973).
5. C. E. Curtis, "Properties of Yttrium Oxide Ceramics", J. Am. Ceram. Soc., **40**[8], 274-278 (1957).
6. J. Krautkrämer and H. Krautkrämer, Ultrasonic Testing of Materials, Springer-Verlag, New York (1983).
7. A. G. Evans and E. A. Charles, "Fracture Toughness Determinations by Indentations", J. Am. Ceram. Soc., **59** [7 - 8] 371-372 (1976).
8. A. S. Wagh, D. Roberts, T. Suratwala, and M. McMann, "Mechanical Properties of Vacuum Sintered Yttria Ceramics", unpublished information.
9. G. A. Gogotsi, "Thermal Stress Behavior of Yttria, Scandia and AlN Ceramics", Ceramurgia Int., **6** [1], 31-35 (1980).
10. W. D. Kingery, H. K. Bowen and D. R. Uhlmann, Introduction to Ceramics, Second ed., John Wiley, New York, pp 786-787 (1960).
11. C. A. Anderson and R. J. Bratton, "Effect of Surface Finish on Hot-Pressed Silicon Nitride"; in NBS Pub., 562, Science of Ceramic

**Machining and Surface Finishing II. Ed. B. J. Hockey and R. W. Rice.
National Bureau of Standards, Washington, DC, (1979).**

- 12. D. P. H. Hasselman, "Elastic Energy of Fracture and Surface Energy as
Design Criteria for Thermal Shock", J. Am. Ceram. Soc., **46** [11], 535-
540 (1963).**

Fig. 1. SEM photomicrograph of fracture surface of CaO-Y₂O₃ composite.

Fig. 2. Thermal shock resistance of CaO-Y₂O₃ Composite.

END

DATE

FILMED

4/6/94