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Thermal Conductivity of Alumina-Toughened Zirconia Composites

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Summary

10-mol% yttria-stabilized zirconia (10YSZ)-alumina composites containing 0 to 30 mol% alumina were fabricated by hot pressing at 1500 °C in vacuum. Thermal conductivity of the composites, determined at various temperatures using a steady-state laser heat flux technique, increased with increase in alumina content. Composites containing 0, 5, and 10-mol% alumina did not show any change in thermal conductivity with temperature. However, those containing 20 and 30-mol% alumina showed a decrease in thermal conductivity with increase in temperature. The measured values of thermal conductivity were in good agreement with those calculated from simple rule of mixtures.

Introduction

A fuel cell is an electrochemical device where the chemical energy of a fuel such as hydrogen is converted into electricity by electrochemical oxidation of the fuel. The only by-products of this process are water and heat. Various types of fuel cells (polymer electrolyte fuel cell, alkaline fuel cell, phosphoric acid fuel cell, methanol fuel cell, molten carbonate fuel cell, and solid oxide fuel cell) are being developed as power sources for a large number of applications. Solid oxide fuel cells[1] (SOFC) offer several advantages over other types of fuel cells such as high efficiency, low emissions, high power density, fuel flexibility, and internal fuel reforming. Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte for high-temperature SOFC because of its high oxide ion conductivity and stability in oxidizing and reducing atmospheres. However, like other ceramic materials, zirconia has low fracture toughness and poor strength. For aeropropulsion applications, the thin electrolyte membrane (10 to 50 μm thick) of the planar anode-supported SOFC needs to be strong and tough as it would be subjected to severe vibrations and thermal cycling during take-off and landing. It has been recently demonstrated[2–4] that the additions of alumina to 10YSZ make it stronger, tougher, lighter, and stiffer at room temperature as well as at 1000 °C. However, no information is available about the thermal conductivity of these composites. The objective of the present study was to investigate the effects of alumina additions on the thermal conductivity of 10YSZ in the SOFC operating temperature region.

Materials and Experimental Methods

The starting materials used were 10 mol% yttria fully-stabilized zirconia powder (HSY–10, average particle size 0.41 μm, specific surface area 5.0 m^2/g) from Daiichi Kigenso Kagaku Kogyo Company, Japan and alumina powder (Baikalox CR–30, 99.99 percent purity, average particle size

0.05 μm, specific surface area 25 m^2/g) from Baikowski International Corporation, Charlotte, North Carolina. Appropriate quantities of 10YSZ powder and alumina powder were slurry mixed in acetone and ball milled for ~24 h using zirconia milling media. Acetone was evaporated and the powder dried in an electric oven. The resulting powder was loaded into a graphite die and hot pressed at 1500 °C in vacuum under 30 MPa pressure into 1 in. diameter discs using a mini-hot press. Grafoil was used as spacers between the specimen and the punches. Load was released before onset of cooling[2,4] after an isothermal hold at high temperature resulting in dense and crack free ceramic composite samples. Residual grafoil from disc surfaces was burned off in air.

Thermal Conductivity Measurement

One inch (25.4 mm) diameter hot pressed discs of 10YSZ-alumina composites were used for thermal conductivity measurements. Thermal conductivity testing of the ceramic materials was carried out using a 3.0 kW CO_2 laser (wavelength 10.6 μm) high-heat flux rig. A schematic diagram of the test rig, photos of the actual test facilities and the general test approach have been described elsewhere.[5] In this steady-state laser heat flux test method, the specimen surface was heated by a laser beam, and backside air-cooling was used to maintain the desired temperature. A uniform laser heat flux was obtained over the 23.9 mm diameter aperture region of the specimen surface by using an integrating ZnSe lens combined with the specimen rotation. Platinum wire flat coils (wire diameter 0.38 mm) were used to form thin air gaps between the top aluminum aperture plate and stainless-steel back plate to minimize the specimen heat losses through the fixture.

Thermal conductivity of ceramic materials, $k_{ceramic}$, can be determined from the pass-through heat flux q_{thru} and measured temperature difference $\Delta T_{ceramic}$ across the ceramic specimen thickness $l_{ceramic}$ under the steady-state laser heating conditions[5]

$$k_{ceramic} = q_{thru} \cdot l_{ceramic}/\Delta T_{ceramic} \tag{1}$$

The actual pass-through heat flux q_{thru} for a given ceramic specimen was obtained by subtracting the laser reflection loss (measured by a 10.6 μm reflectometer) and the calculated radiation heat loss (total emissivity was taken as 0.50 for the oxides) at the ceramic surface from the laser delivered heat flux (i.e., $q_{thru} = q_{delivered} - q_{reflected} - q_{radiated}$). Note that the non-reflected laser energy is absorbed at or near the specimen surfaces because of the quite high emissivity at the 10.6 μm laser wavelength region for the oxides. In some test cases, the pass-through heat flux q_{thru} was verified with an internal heat flux gauge incorporated with the substrates (instrumented specimens) via an embedded miniature thermocouple. For the hot pressed bulk specimens, the temperature difference $\Delta T_{ceramic}$ in the ceramic was directly measured by using two 8μm pyrometers at both specimen front heating and back side air cooling surfaces.

Results and Discussion

Compositions of various 10YSZ-alumina composites used in this study and their densities, ρ, are presented in table I. The specimens are at least 99 percent dense. Density decreased with increase in alumina content, as expected. X-ray diffraction patterns from various 10YSZ-alumina composites are shown in figure 1. Cubic zirconia and α-alumina were the only phases present indicating the absence of any chemical reaction between the constituent materials during hot pressing at elevated temperatures. Typical SEM micrographs taken from the polished cross-sections of various YSZ/alumina composites are shown in figure 2. Alumina particulates are uniformly dispersed throughout the material. The dark areas represent alumina while the light areas indicate the 10YSZ matrix, as confirmed from EDS analysis (fig. 3). TEM micrograph and dot maps for various elements for the composite containing 30 mol%

alumina are shown in figure 4. The average equiaxed grain size is less than 1.0 μm for either YSZ matrix or alumina. The high magnification TEM micrographs showing grain boundaries and triple junctions for the 0 and 30 mol% alumina composites are presented in figures 5 and 6, respectively. The grain boundaries as well as the triple junctions are clean for either composite, indicating the absence of any amorphous phase. No appreciable deformation or microcracks of adjacent grains in the composites, which might occur due to thermoelastic mismatches between the YSZ matrix and the alumina particulates, was observed from the analysis of TEM micrographs.

Table I.—Compositions of 10YSZ-alumina composites

Sample No.	Composition (mol%)		Density, ρ (g/cm^3)
	10YSZ	Al_2O_3	
A2-0	100	0	6.09 ± 0.05
A2-5	95	5	5.89 ± 0.01
A2-10	90	10	5.80 ± 0.01
A2-20	80	20	5.57 ± 0.01
A2-30	70	30	5.38 ± 0.04
Al_2O_3	0	100	3.94 ± 0.03

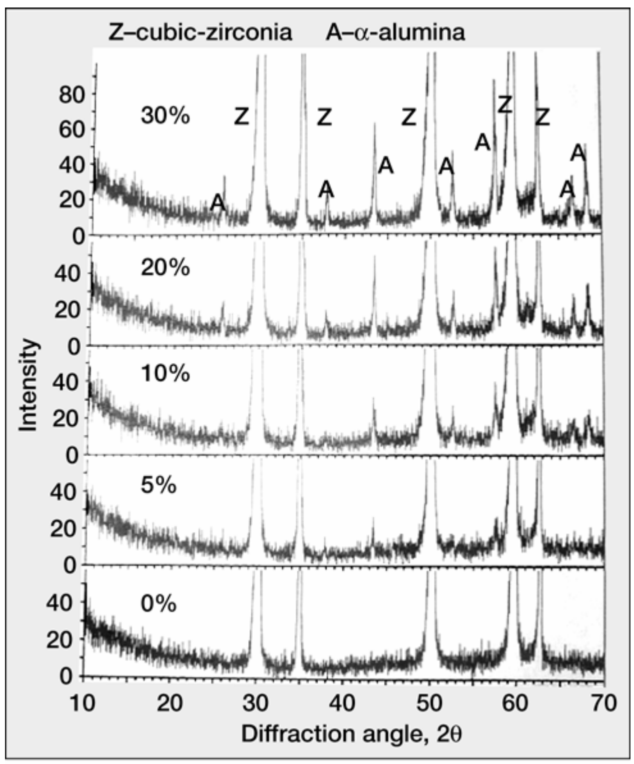


Figure 1.—X-ray diffraction patterns for 10YSZ reinforced with different alumina contents as indicated. "Z" and "A" indicate cubic-zirconia and α-alumina, respectively.

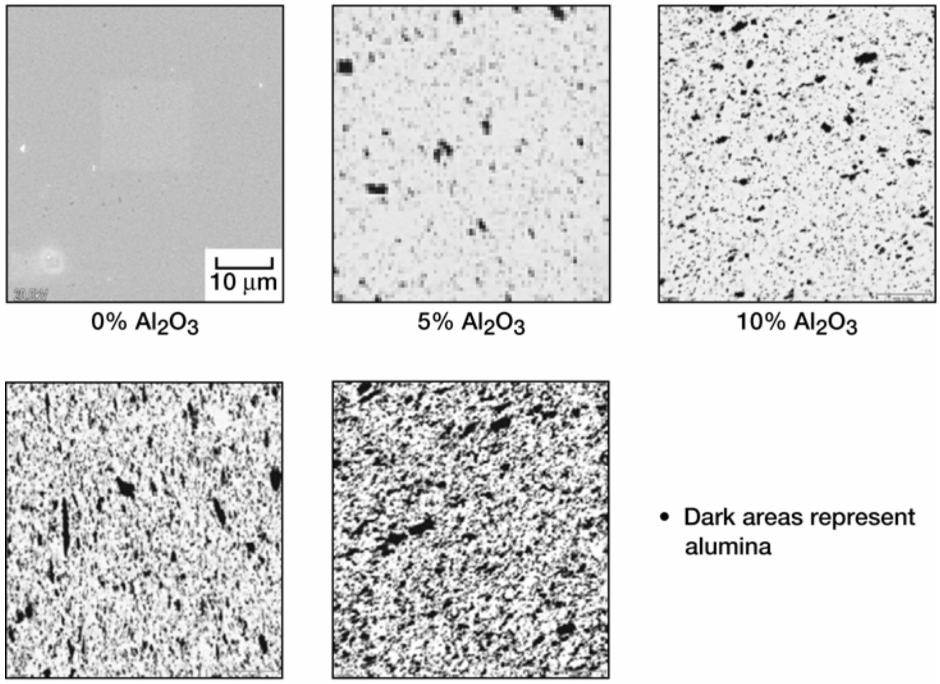


Figure 2.—SEM micrographs showing polished cross-sections of 10YSZ-alumina composites containing various alumina mol%.

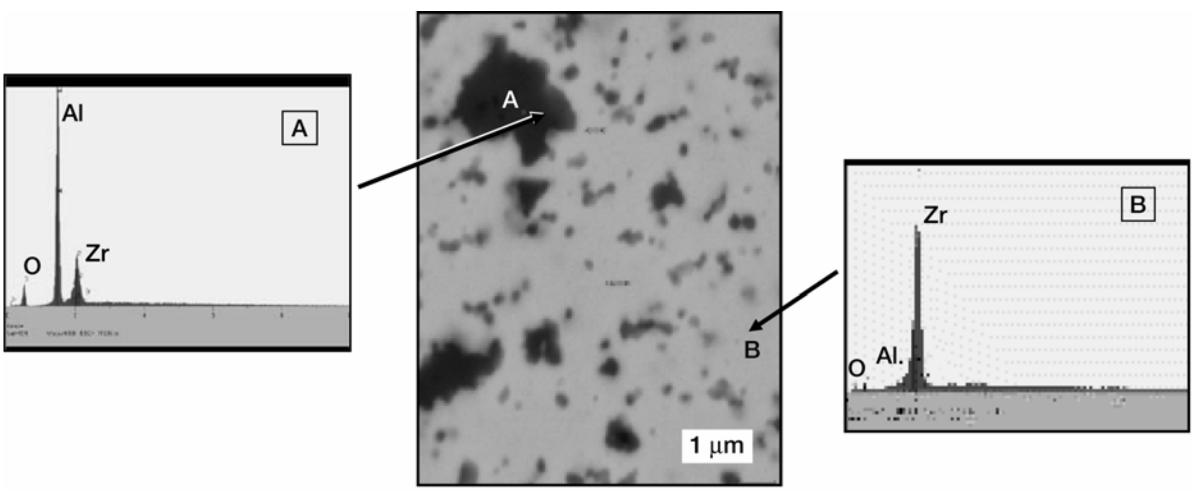


Figure 3.—SEM micrograph and EDS analysis of 10YSZ-alumina composite containing 10 mol% alumina; dark area (A): alumina, light area (B): zirconia.

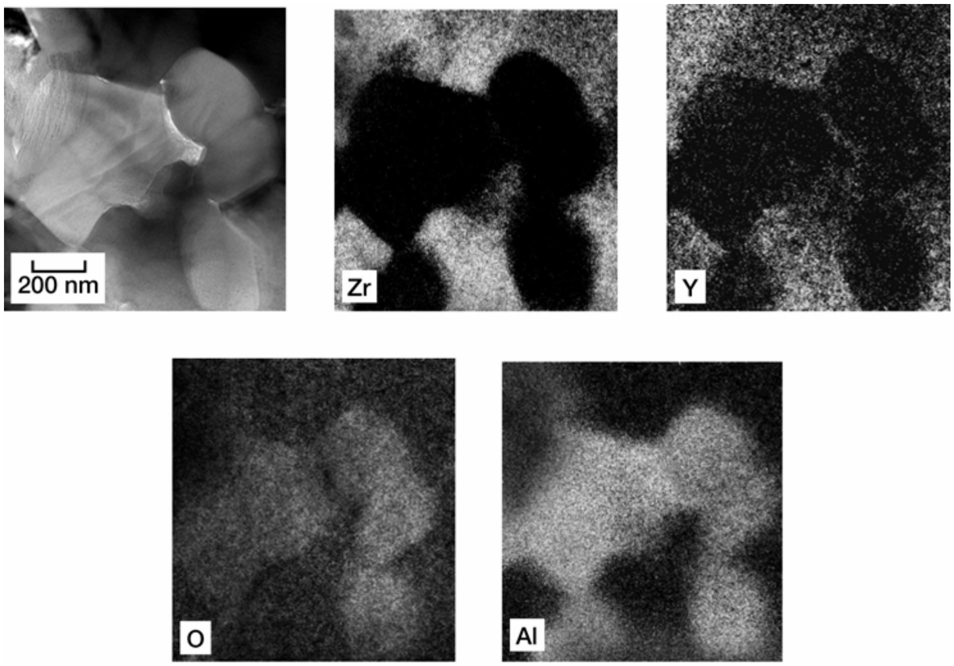
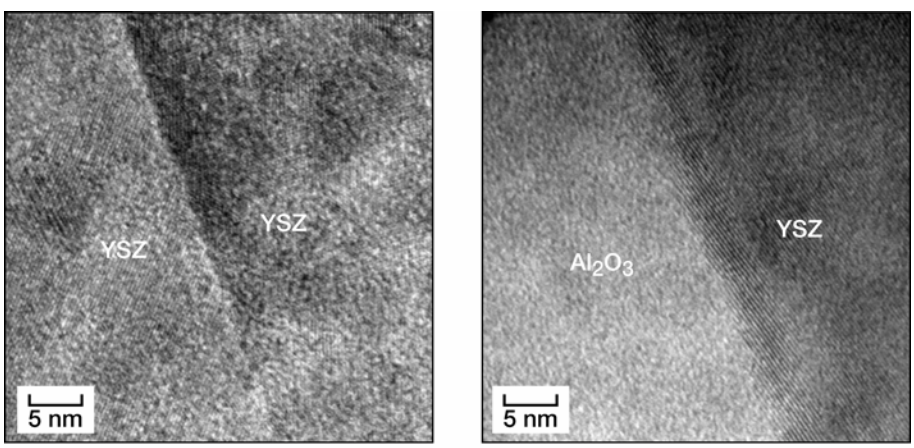


Figure 4.—TEM micrograph showing zirconia and alumina grains and dot maps of different elements for 10YSZ-alumina composite containing 30 mol% alumina.



0 mol% Al_2O_3 30 mol% Al_2O_3

Figure 5.—High magnification TEM micrographs showing grain boundaries in 10YSZ-alumina composites containing 0 or 30 mol% alumina.

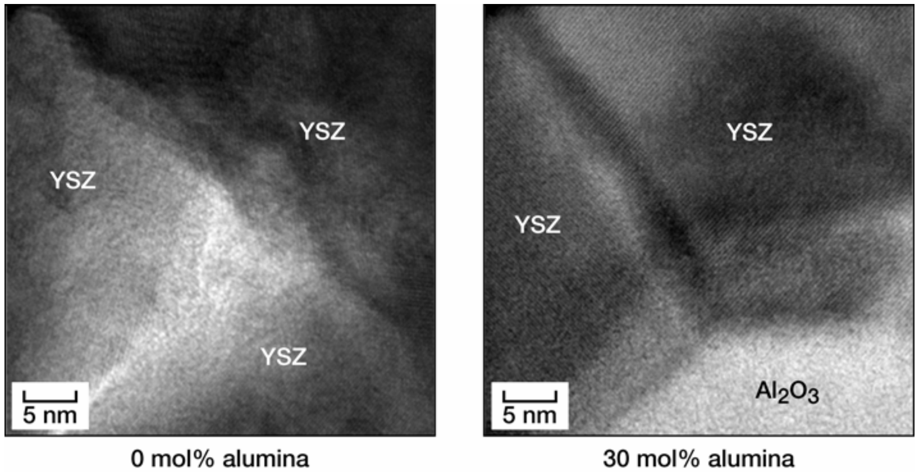


Figure 6.—High magnification TEM micrographs showing triple junctions in 10YSZ-alumina composites containing 0 or 30 mol% alumina.

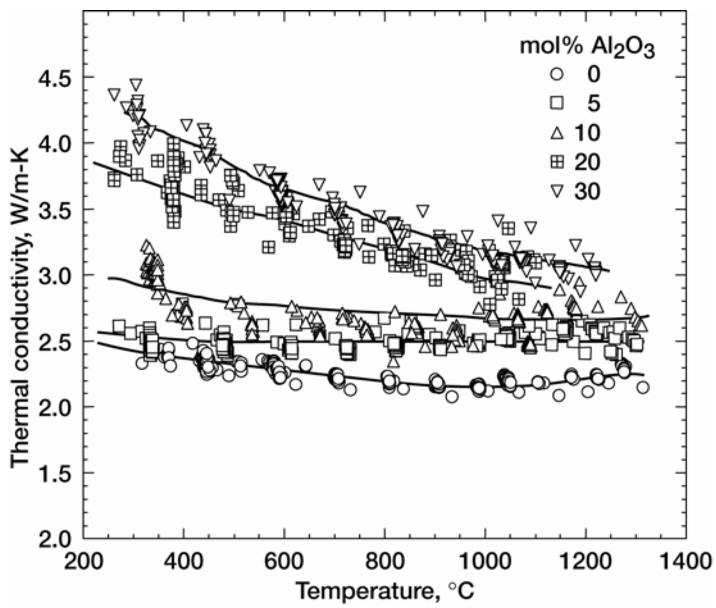


Figure 7.—Temperature dependence of thermal conductivity of 10YSZ-alumina composites containing 0, 5, 10, 20, or 30 mol% alumina determined by a steady-state laser heat flux technique.

Thermal conductivities of hot pressed specimens of 10YSZ-alumina composites of various compositions, as a function of temperature, are shown in figure 7. Results for 10YSZ and alumina are also shown for comparison. Data for alumina shows a large scatter particularly in the low temperature region. As alumina has much higher thermal conductivity at low temperatures, the precision of steady-state laser technique, used in the current study, is not as good due to small thermal gradient across the test specimen at low temperatures. Thicker test specimens of alumina may improve the precision. Thermal conductivity increased with increase in alumina content. This is expected, as the thermal conductivity of alumina is much higher[12] than that of 10YSZ. The increase in thermal conductivity with alumina additions is more significant at lower temperatures than at higher temperatures. Thermal conductivity of composites containing 0, 5, and 10-mol% alumina exhibited slight changes with temperature. However, those containing 20 and 30-mol% alumina showed a sharper decrease in thermal conductivity with increase in temperature.

Microstructures of composites of various compositions (fig. 2) show that alumina phase is uniformly dispersed within the major continuous 10YSZ phase. For materials with such a microstructure, when thermal conductivity of the dispersed phase (alumina) is much higher than that of the continuous phase (10YSZ), the thermal conductivity of the composite (k_c) is given by[10]

$$k_c = k_{10YSZ}\,[(1 + 2V_{Al2O3})/(1 - V_{Al2O3})] \tag{2}$$

where k represents the thermal conductivity and V the volume fraction. Thermal conductivity of the composites was also calculated using the simple rule of mixtures:

$$k_c = (k_{10YSZ}\,.\,V_{10YSZ}) + (k_{Al2O3}\,.\,V_{Al2O3}) \tag{3}$$

Thermal conductivity of various 10YSZ-alumina composites at 1000 °C were calculated from Eqs. (2) and (3) using values of 2.15 and 6.88 W/m-K for thermal conductivity of 10YSZ and alumina, respectively, measured in the current study. The calculated and measured values are compared in table II. The measured values of thermal conductivity of 10YSZ-alumina mixtures are in much better agreement with those calculated from the rule of mixtures Eq. (3), rather than from Eq. (2).

Thermal conductivity of alumina from various studies is compared in figure 8. Results of the present study are in good agreement with those reported by other researchers, particularly at high temperatures. However, values reported by Santos and Taylor[11] are high compared with other studies. Literature values of thermal conductivity of yttria-stabilized zirconia containing various mol% of the stabilizer are shown in figure 9, along with the results of the current study for 10 mol% (16.9 wt%) yttria containing zirconia. Significant variation is seen in the results for different compositions due to different microstructures resulting from various amounts of yttria stabilizer. Thermal conductivity of zirconia decreases with increase in yttria content up to 5.12 mol% (9 wt%). However, thermal conductivity increased for compositions containing higher yttria content. The 3YSZ consists almost entirely of tetragonal (*t*) phase.[15] Compositions containing >3 mol% (5.3 wt%) yttria contain a significant amount of the monoclinic (*m*) phase and the microstructure consists of a two-phase mixture of *t* and *m* phases. The 10YSZ composition of the present study, containing 10 mol% (16.9 wt%) yttria, is fully stabilized and consists of the cubic phase of zirconia.

Table II.—Measured and calculated thermal conductivities of 10YSZ-alumina composites at 1000 °C

Sample No.	Composition (mol%)		Thermal conductivity (W/m-K) at 1000 °C		
	10YSZ	Al_2O_3	Measured (This study)	Calculated from Eq. (2)	Calculated from Eq. (3)
A2-0	100	0	2.2	--	--
A2-5	95	5	2.5	2.5	2.4
A2-10	90	10	2.7	3.0	2.7
A2-20	80	20	3.0	4.0	3.2
A2-30	70	30	3.3	5.3	3.7
Al_2O_3	0	100	6.9	--	--

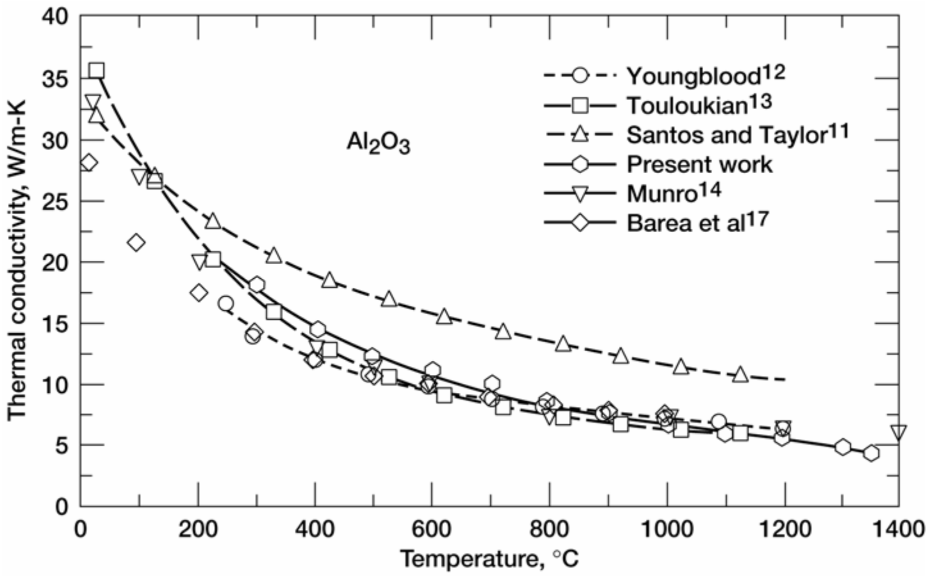


Figure 8.—Thermal conductivity of alumina from various studies.

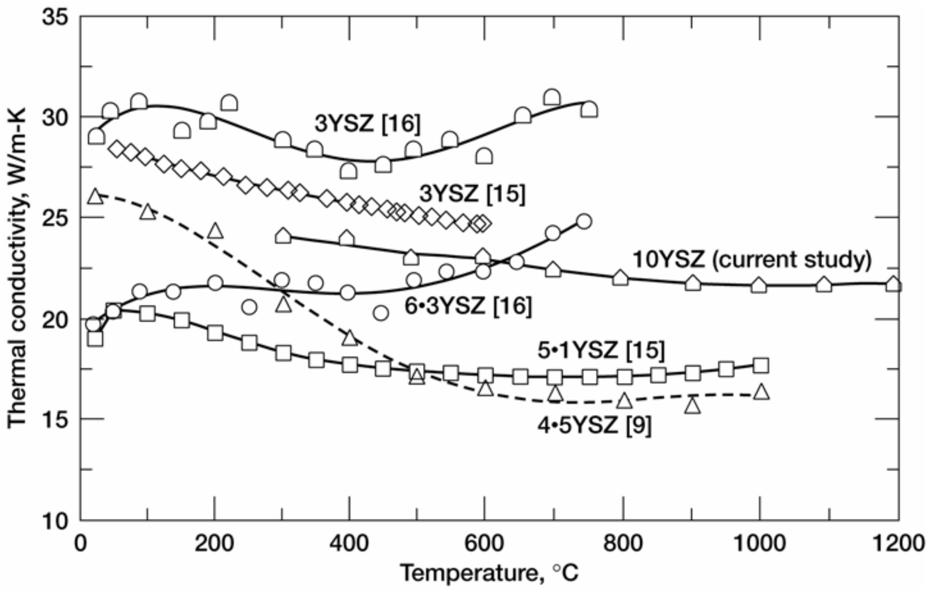


Figure 9.—Thermal conductivity of zirconia containing different mol% of yttria content.

Summary

Thermal conductivity of 10YSZ-alumina composites containing 0 to 30 mol% alumina has been determined as a function of temperature. Thermal conductivity increased with an increase in alumina content. Thermal conductivity showed slight change with temperature for 0, 5, and 10 mol% alumina compositions whereas it decreased with temperature for composites containing 20 and 30 mol% alumina. The measured thermal conductivity values are in good agreement with those calculated from simple rule of mixtures.

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13. ABSTRACT ***(Maximum 200 words)***

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