Thermal Properties of Porous Ni/YSZ Particulate Composites at High Temperatures

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The porosity, composition, and temperature dependence of thermal properties in porous Ni/yttria-stabilized zirconia (YSZ) cermet has been investigated at high temperatures by the laser flash diffusivity method. At a temperature range of 1073 to 1273 K, there is no temperature dependence of thermal diffusivity of the cermets. Observable, however, is a slight increase in both of specific heat and thermal conductivity with an increase in temperature. Although the specific heat is governed by the law of mixing in composition, it is independent of the porosity. Pores in the cermet act as heat barriers to prevent heat transfer, in which thermal conductivity is regarded as zero. The relationship between thermal conductivity and porosity can be expressed by the resultant conductivity calculated on the basis of the modified effective medium theory. In this calculation, a porous Ni/YSZ cermet is regarded as a simple cubic resistance network composed of two kinds of unit resistors corresponding to the solid and pore phases. Moreover, the composition dependence of the thermal conductivity of a dense Ni/YSZ cermet could be expressed using the resultant conductivity of the resistance network of unit resistors corresponding to Ni and YSZ. On the basis of these results, the following equation expressing the thermal conductivity of porous Ni/YSZ cermets $\lambda_c/\text{Wm}^{-1}\text{K}^{-1}$, has been derived as a function of Ni-volume fraction for total solids V_{Ni} and porosity P , for 1273 K

$$\lambda_c = \frac{1}{8} \{K_A + (K_A^2 + K_B)^{1/2}\} (1-P)(2-3P), \quad \left(0 \leq P < \frac{2}{3}\right)$$

where $K_A/\text{Wm}^{-1}\text{K}^{-1} = 0.16 - 55.62V_{\text{Ni}} + 195.7V_{\text{Ni}}^2$, $K_B/(\text{Wm}^{-1}\text{K}^{-1})^2 = 95.23 + 1432.3V_{\text{Ni}} + 1257V_{\text{Ni}}^2$. The validity is confirmed.

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I. Introduction

Electric power generation technologies which are both highly efficient and environmentally benign in an economical way are of high importance. The solid oxide fuel cell (SOFC) has special advantages in respect to these requirements because of its high energy conversion efficiency without utilizing any noble metal catalysts. A SOFC basically consists of two electrodes (anode and cathode) separated by an electrolyte. Practical SOFCs are connected in electrical series to build voltage. The anode materials for SOFCs must have high electro-catalytic oxidation activity for fuels and must be chemically stable in a high temperature reduction atmosphere. A porous Ni/yttria-stabilized zirconia (YSZ) satisfying these requirements is generally used as the anode in the SOFCs, having YSZ as the electrolyte⁽¹⁾. By mixing YSZ with Ni, the sintering of Ni particles can be prevented, and the difference in thermal expansion coefficient between the anode and the electrolyte can be reduced⁽²⁾⁽³⁾.

SOFCs are generally operated at high temperatures (about 1273 K). The high operating temperatures promote rapid reaction kinetics, allows reforming of hydrocarbon fuels within the anode, and produce high quality byproduct heat suitable for use in cogeneration

or in bottoming cycle. In this case, endothermic reactions (the steam reforming reactions of hydrocarbons) and exothermic reactions (the oxidizing reactions of H_2 and CO) take place concomitantly in the anode. Accordingly, a complex temperature distribution is formed to generate a complex thermal stress within the cell components.

Recently, results of computational simulations of temperature and thermal stress distributions formed within cells, obtained using the finite element method have been reported⁽⁴⁾⁻⁽⁹⁾. In these simulations, data on thermal properties such as specific heat and the thermal conductivity of all cell component materials are indispensable. The experimental values of the thermal property data of porous Ni/YSZ cermets, however, have not yet been reported. Estimated values have therefore been used⁽⁴⁾⁻⁽⁶⁾, or the influence of the anode has been ignored⁽⁷⁾⁻⁽⁹⁾ in the simulations. In this paper, the specific heat, thermal diffusivity, and thermal conductivity of porous Ni/YSZ cermets have been measured at high temperatures, and the values of these thermal properties related to composition and porosity have been examined. Moreover, an expression of the thermal conductivity has been derived as a function of composition and porosity.

II. Experimental

Ni/YSZ cermets were prepared according to the following procedures. Weighed NiO powder or Ni powder (Soekawa-Rikagaku, purity 99.9 mass%) and YSZ powder (TOSOH, TZ-8Y, ZrO_2 -8 mol% Y_2O_3) in appropriate ratios were mixed and milled for 86.4 ks (24 h) with Y-TZP (yttria-stabilized tetragonal zirconia polycrystal) balls. These mixtures were pressed at 100 MPa into disks with a diameter of 23 mm and a thickness of 5 mm, and then sintered at 1723 K for 21.6 ks (6 h) in the atmosphere or in a reducing-gas mixture of N_2 -4% H_2 . The NiO in the cermet was reduced to metallic Ni by exposing the samples to the reducing gas mixture for 43.2 ks (12 h). The specimens with a diameter of 10 mm and a thickness of 1 mm were cut from the disks. The volume fraction of Ni and YSZ for total solids and the porosity of the samples used in this measurement are shown in Table 1. These values were calculated from (a) the theoretical density, which was obtained from the chemical composition and the assumption that Ni and YSZ were simply mixed, and (b) the apparent density.

The specific heat and thermal diffusivity were measured by the laser flash diffusivity method using a Shinku-Riko type TC-3000. A 3 J/pulse ruby laser was used as the heat source, with a pulse width of 800 μs . The experiments were conducted in a vacuum (1.33 Pa) in a temperature range of 1073 to 1273 K. Sapphire was used as the standard sample to obtain the specific heat. The thermal conductivity was calculated from the specific heat, density, and thermal diffusivity.

Table 1 Specifications of porous Ni/YSZ cermet samples studied.

No.	Ni-volume fraction for total solid	YSZ-volume fraction for total solid	Density ($\times 10^3 \text{ kg/m}^3$)	Porosity
1	0.00	1.00	5.932	0.00
2	0.10	0.90	5.283	0.15
3	0.22	0.78	5.551	0.15
4	0.32	0.68	5.581	0.18
5	0.44	0.56	5.438	0.24
6	0.44	0.56	4.952	0.31
7	0.44	0.56	4.292	0.40
8	0.44	0.56	4.243	0.41
9	0.44	0.56	3.798	0.47
10	0.44	0.56	3.401	0.52
11	0.54	0.46	6.340	0.18
12	0.54	0.46	5.887	0.24
13	0.54	0.46	5.516	0.28
14	0.63	0.37	6.094	0.18
15	0.63	0.37	5.860	0.22
16	0.63	0.37	5.397	0.28
17	0.72	0.28	7.609	0.04
18	0.72	0.28	6.128	0.23
19	0.72	0.28	5.486	0.31
20	1.00	0.00	8.895	0.00
21	1.00	0.00	7.712	0.13
22	1.00	0.00	6.217	0.30

III. Results

1. Specific heat

The temperature dependence of the specific heat of porous Ni/YSZ cermets with different Ni-volume fractions for total solids is shown in Fig. 1. Whatever the composition, the specific heat changed linearly according to temperature and presented positive temperature coefficients. These values, however, were so small that the changes in specific heat between 1073 and 1273 K were less than 3%. In addition, the specific heat decreased with increasing the Ni-volume fraction. The obtained specific heat of Ni agrees well with the experimental values elucidated by Hultgren and Land⁽¹⁰⁾. The composition dependence of the specific heat is shown in Fig. 2 where the Ni concentration is represented in mass%. A linear relationship could be observed between specific heat and Ni concentration. The lines in Fig. 2 indicate the law of mixing as expressed by eq. (1) at each temperature.

$$C_C = [\text{mass\% YSZ}] \times C_{\text{YSZ}}/100 + [\text{mass\% Ni}] \times C_{\text{Ni}}/100 \quad (1)$$

where C_C , C_{YSZ} , and C_{Ni} are specific heats of the cermet, of YSZ, and of Ni, respectively. All the data points contiguously situated on the respective lines thus show that the law of mixing can be applied to composition dependence.

The relationship between the specific heat and porosity of Ni/YSZ cermets with Ni-volume fraction for total solids of 0.44, 0.72, and 1.00 is shown in Fig. 3. The specific heat was independent of the porosity at any Ni-volume fraction. The law of mixing, however, holds the specific heat. The reason is because Ni/YSZ cermet is a simple mixture of Ni and YSZ without any compounds, the specific heat of the pore is negligible, and the pore does not contribute to the mass.

Fig. 1 Temperature dependence of specific heat (C_p) of Ni/YSZ cermet from 1073 to 1273 K with Ni-volume fraction for total solids (V_{Ni}): 0.00, 0.32, 0.54, 0.72, 1.00. The numbers in the brackets correspond to the sample numbers in Table 1.

Fig. 2 Composition dependence of specific heat (C_p) of Ni/YSZ cermet with mass%Ni of 0 to 100 at 1073, 1173, and 1273 K. Straight lines represent the law of mixing at each temperature. The numbers close to marks correspond to the sample numbers in Table 1.

Fig. 3 Porosity dependence of specific heat (C_p) of Ni/YSZ cermet at 1273 K with Ni-volume fraction for total solids (V_{Ni}): 0.44, 0.72, 1.00.

2. Thermal diffusivity

The temperature dependence of the thermal diffusivity of Ni/YSZ cermets is given in Fig. 4. The thermal diffusivity of Ni was about 20 times that of YSZ, and the thermal diffusivity of Ni/YSZ cermets rose with the increase in the Ni-volume fraction. In any composition, however, no temperature dependence can be observed between 1073 to 1273 K. The present experimental results of Ni agree well with the literature data by Zinovyev *et al.*⁽¹¹⁾, and those of YSZ also agree with the data of $ZrO_2-5.1$ mol% Y_2O_3 by Hasselman *et al.*⁽¹²⁾.

The thermal diffusivity at 1273 K for various Ni concentrations as a function of porosity is shown in Fig. 5. The decrease of thermal diffusivity indicates that the pores in the cermet are thermal barriers against heat transfer.

3. Thermal conductivity

Thermal conductivity rather than thermal diffusivity is generally used in materials science. Thermal conductivity λ can be expressed by the following equation.

$$\lambda = \alpha \times d \times C \quad (2)$$

Fig. 4 Temperature dependence of thermal diffusivity (α) of Ni/YSZ cermet from 1073 to 1273 K with Ni-volume fraction for total solids (V_{Ni}): 0.00, 0.32, 0.54, 0.72, 1.00. The numbers in the brackets correspond to the sample numbers in Table 1.

Fig. 5 Porosity dependence of thermal diffusivity (α) of Ni/YSZ cermet at 1273 K with Ni-volume fraction for total solids (V_{Ni}): 0.44, 0.72, 1.00.

where α , d , and C are thermal diffusivity, density, and specific heat, respectively. The relationship between thermal conductivity calculated by eq. (2) and temperature is shown in Fig. 6. During the calculation, the change in the density of Ni/YSZ cermet attributable to thermal expansion was considered, but was found to be insignificant at less than 5%. The thermal conductivity of the cermet became larger as the Ni concentration increased and that of Ni agrees well with the experimental values by Binkele⁽¹³⁾. Hasselman⁽¹²⁾ *et al.* have reported that the thermal conductivity of YSZ (10 mol% Y_2O_3) is $2.0 \text{ Wm}^{-1} \text{ K}^{-1}$ for 873 K and Garvie⁽¹⁴⁾ has reported that the thermal conductivity of calcia-stabilized zirconia (about 20 mol% CaO) is $2.7 \text{ Wm}^{-1} \text{ K}^{-1}$ for 1073 K and $2.8 \text{ Wm}^{-1} \text{ K}^{-1}$ for 1273 K. The present data for 1073 to 1273 K agree with these literature data. Moreover, whatever the com-

Fig. 6 Temperature dependence of thermal conductivity (λ) of Ni/YSZ cermet from 1073 to 1273 K with Ni-volume fraction for total solids (V_{Ni}): 0.00, 0.32, 0.54, 0.72, 1.00. The numbers in the brackets correspond to the sample numbers in Table 1.

position, the thermal conductivity of the cermet varied linearly with respect to the temperatures and presented slightly positive temperature coefficients. The temperature dependence of the cermet represents a direct reflection of that of the specific heat because of the absence of the temperature dependence of the thermal diffusivity.

The porosity dependence of the thermal conductivity of Ni/YSZ cermets is shown in Fig. 7. A remarkable decrease in the thermal conductivity with an increased

Fig. 7 Porosity dependence of thermal conductivity (λ_p) of Ni/YSZ cermet at 1273 K with Ni-volume fraction for total solids (V_{Ni}): 0.44, 0.72, 1.00. The long-dashed, short-dashed, and dotted lines represent predictions for V_{Ni} : 1.00 by Eucken's, Russell's, and Franci-Kingery's equations, respectively. Solid lines represent predictions by the modified effective-medium theory.

porosity could be observed, which was caused by the pore acting as a thermal barrier.

In the simulation of the temperature distribution in SOFCs, a estimated value ($3 \text{ Wm}^{-1} \text{ K}^{-1}$ at 1073–1273 K)⁽¹⁵⁾ is generally used for the thermal conductivity of the Ni/YSZ cermet anode⁽⁵⁾⁽⁶⁾. As is clear, from the present study, however, the composition and porosity dependence of the thermal conductivity are so great that the application of this estimated value may produce a simulation much different from the actual temperature distribution.

IV. Discussion

1. Effect of pore phase on thermal conductivity

Inasmuch as heat transfer flux components, arising from various mechanisms and associated with pore phase are assumed to be independent, the thermal conductivity of the pore phase λ_{po} can be approximated by⁽¹⁶⁾

$$\lambda_{po} = \lambda_{po}^{cond} + \lambda_{po}^{rad} + \lambda_{po}^{conv} + \lambda_{po}^i \quad (3)$$

where the components appearing on the right-hand side refer to the gas conductivity, thermal radiation between the walls, gas convection, and heterogeneous physico-chemical process, respectively, occurring at gas-solid interfaces. The thermal conductivity in the present study was determined in a vacuum (1.33 Pa) which makes the first and third terms negligible. Moreover, the absence of any reaction at gas-solid interfaces also makes the fourth term negligible. Accordingly, to be considered for the thermal conductivity of pore phase is the thermal radiation between the walls.

The thermal radiation of the closed pore λ_{cpo}^{rad} can be expressed by⁽¹⁷⁾

$$\lambda_{cpo}^{rad} = 4f\xi\sigma T^3\delta \quad (4)$$

where σ , ξ , T , δ , and f , respectively, are the Stephan-Boltzman constant ($5.73 \times 10^{-8} \text{ Jm}^{-2} \text{ s}^{-1} \text{ K}^{-1}$), the emissivity of pore walls, the absolute temperature, the pore size and the pore radiation factor which can be determined by the geometric shape of the pore, and ranges from 0 to 1.

The SEM observation indicated $\delta = 1 \sim 3 \mu\text{m}$ ⁽³²⁾. The emissivity of Ni which varies with temperature and wavelength is $0.1 \sim 0.3$ ⁽¹⁸⁾ over the temperature range of 1073 to 1273 K. Although to date no data exist on the emissivity of YSZ, it is reported that the emissivity of calcia-stabilized zirconia is $0.25 \sim 0.35$ ⁽¹⁹⁾ in the temperature range. If the larger of the above data are substituted into eq. (4), and if we assume $f=1$, λ_{cpo}^{rad} for 1273 K is estimated to be $5 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-1}$.

The open pore, however, is to be considered rather than the closed pore because the anode is a type of gas-diffusion electrode. Savvides and Goldsmid⁽²⁰⁾ presented an expression for the radiative thermal open-pore conductivity under the assumption that the wavelength of photon > the photon mean free path length

$$\lambda_{opo}^{rad} = 4\sigma T^3 L' P_O \quad (5)$$

where L' and P_O are the effective open-pore length (= the photon mean free path) and the open-pore volume fraction, respectively. The conductivity is estimated to be only $0.24 \text{ Wm}^{-1} \text{ K}^{-1}$ even if the effective length equals the thickness of the sample (1 mm) for $P_O=0.50$ and $T=1273 \text{ K}$. This estimation is an extreme case because the actual effective length will be much shorter than 1mm. The thermal conductivity of the open-pore phase is, therefore, much less than $0.24 \text{ Wm}^{-1} \text{ K}^{-1}$. Thus, the thermal conductivity of the pore phase is so small compared with all experimental values of the thermal conductivity of the cermet that the heat transfer through the pore phase can be negligible.

2. Derivation of an expression for the thermal conductivity of porous Ni/YSZ cermets

An attempt will be made to express the thermal conductivity of porous Ni/YSZ cermets as a function of porosity and composition. The equation for the thermal conductivity of porous Ni/YSZ cermets is derived by applying an expression for the conductivity of two-phase materials in the three stages: (1) the derivation of the equation for the thermal conductivity of the solid phase with different compositions as a function of porosity, (2) the derivation of the equation for the thermal conductivity of the solid phase as a function of its composition, and (3) the deviation of the equation for the thermal conductivity of porous Ni/YSZ cermets as a function of their composition and porosity by combining the results of (1) and (2). The phased application of an expression for the conductivity of two-phase materials are reasonable because the thermal conductivity of the pore phase is much smaller than that of Ni and YSZ.

First, although the porous Ni/YSZ cermet is composed of three phases: Ni, YSZ, and pore phase, it is regarded as consisting of two phases: solid and pore. Of the previously published theories on the calculation of

conductivity of two-phase materials, the most generally employed are the expressions by Eucken⁽²¹⁾ and by Russell⁽²²⁾. Both were derived from Maxwell's relationship for conductors and resistors. Eucken and Russell assumed that at a coarse scale a heterogeneous composite material consisting of a continuous phase and a dispersed phase may be viewed as an effective homogeneous medium. Loeb⁽²³⁾ has derived an equation relating thermal conductivity with the porosity and pore size, pore shape, and emissivity of the pore. Moreover, Franci and Kingery⁽²⁴⁾ have reported that the thermal conductivity of the porous body was related to the conductivity of the solid phase to a good approximation by a linear function of porosity. This equals Loeb's equation when the heat transfer through the pore is negligible. These equations are listed in Table 2.

The calculated values of the thermal conductivity by the above theoretical expressions in the case of Ni-volume fraction for total solids, $V_{Ni}=1.00$, are also presented in Fig. 7. The experimental data are considerably lower than the calculated values. One reason for the deviation is that most of the pores in the cermet are open pores. Moreover, the reason why the classical models often do not work is that they fail to take into account the porous-structure geometry and the structure of the contacts between particles composing real materials⁽¹⁷⁾. These elements which characterize the structure of porous materials usually constitute merely a small part of their total porosity. These elements, however, provide a significant contribution to the thermal resistance of any macroscopic volume element subjected to a heat flux, and thus diminish thermal conductivity.

A simple but powerful theoretical description of the conductivity of disordered resistance networks has been provided in the "effective medium theory"⁽²⁵⁾⁽²⁶⁾, and found to be an accurate approximation to the bond percolation model. The theory has been applied in predicting physical constants, such as the electrical and mechanical properties of two-phase materials⁽²⁷⁾⁻⁽³¹⁾. In a preceding

Table 2 Equations for thermal conductivity of two-phase materials.

Eucken:	$\lambda_c = \frac{(1+2V_A)Q+2V_B}{(2+V_A)+V_BQ} \lambda_B$	λ_c =conductivity of two phase material
Russell:	$\lambda_c = \frac{(1-V_A^{2/3})+V_A^{2/3}Q}{(1-V_A^{2/3}+V_A)+(V_A^{2/3}-V_A)Q} \lambda_B$	λ_A =conductivity of phase A
Leob:	$\lambda_p = \left[(1-P_C) + \frac{P_C}{\frac{4\sigma f \xi T^3 \delta}{P_L \lambda_S} + (1-P_L)} \right] \lambda_S$	λ_B =conductivity of phase B
Franci & Kingery:	$\lambda_p = (1-P_C)\lambda_S$	λ_p =conductivity of porous sample
Yuge:	$\lambda_c = \frac{1}{4} \left[(3V_A-1)\lambda_{mA} + (3V_B-1)\lambda_{mB} + \{((3V_A-1)\lambda_{mA} + (3V_B-1)\lambda_{mB})^2 + 8\lambda_{mA}\lambda_{mB}\}^{1/2} \right]$	λ_S =conductivity of solid phase
		$Q = \lambda_A / \lambda_B$
		$\lambda_{mA} = V_A \lambda_A + V_B \lambda_{AB}$
		$\lambda_{mB} = V_B \lambda_B + V_A \lambda_{AB}$
		$\lambda_{AB} = 2\lambda_A \lambda_B / (\lambda_A + \lambda_B)$
		V_A =volume fraction of phase A
		V_B =volume fraction of phase B
		P_C =cross-sectional porosity
		P_L =longitudinal porosity
		σ =Stefan-Boltzman constant
		f =geometrical pore factor
		ξ =emissivity
		T =absolute temperature
		δ =dimension of pore

paper⁽³²⁾ we have reported that the electrical conduction path formation by Ni particles in Ni/YSZ cermets is explained by a site percolation model for a simple cubic lattice. Yuge⁽³³⁾ has modified the effective-medium theory to derive an expression for the thermal conductivity of two-phase materials correlated to site percolation on a simple cubic lattice. He has shown the expression's validity for glass particle-silicon rubber, glass fiber-plastic, and air-saturated porous sandstone and fire brick despite the absence of consideration for porous-structure geometry and the structure of between-phase contacts. The derived equation is also presented in Table 2.

The solid lines in Fig. 7 are obtained by substituting the experimental data of dense Ni and zero for the thermal conductivity of the pore phase to eq. (6) in the case of $V_{\text{Ni}}=1.00$, and by fitting the experimental data to eq. (6), regarding λ_s as the fitting parameter in the case of $V_{\text{Ni}}=0.44$ and $=0.72$. The experimental data follows eq. (6) which is derived from the modified effective-medium theory (MEMT)⁽³³⁾.

$$\lambda_c = \frac{1}{2} \lambda_s (1-P)(2-3P), \quad \left(0 \leq P < \frac{2}{3}\right) \quad (6)$$

where λ_c , λ_s and P are the thermal conductivity of the porous cermet, the solid phase, and the porosity, respectively.

Next performed is an investigation of the composition dependence of the solid-phase thermal conductivity. The solid-phase thermal conductivity related to the volume fraction of Ni for total solids is shown in Fig. 8. In this figure, the experimental data are adopted at the Ni-volume fraction of 0.00 and 1.00, and except for the two data, the estimated values obtained by fitting the experimental data to eq. (6) regarding λ_s as the fitting parameter at each Ni-volume fraction are adopted be-

cause experimental data are not available. The error bars represent the statistical errors in the curve fitting to eq. (6). The increase in thermal conductivity with increasing the Ni-volume fraction to 0.32 is small, but above 0.32 it increases rapidly with increasing the Ni-volume fraction. This is caused by the Ni particles' forming a network above the volume fraction of Ni.

The calculated values by the theories of Eucken and Russell are also presented. These values are obtained under the condition that (a) YSZ is the matrix phase and Ni is the dispersed phase, and (b) is the reverse of (a). For (a), although both predictions agree with the experimental values up to 0.32 Ni-volume fraction where Ni particles are mutually isolated, the predictions deviate markedly from the experimental values above 0.32 Ni-volume fraction where a continuous Ni phase is formed. Moreover, for (b), both predictions deviate considerably from the experimental values for all compositions.

The solid-phase thermal conductivity can be expressed the following equation which is derived based on MEMT:

$$\lambda_s = \frac{1}{4} \{K_A + (K_A^2 + K_B)^{1/2}\} \quad (7)$$

where $K_A/\text{Wm}^{-1}\text{K}^{-1} = 0.16 - 55.62V_{\text{Ni}} + 195.7V_{\text{Ni}}^2$, $K_B/(\text{Wm}^{-1}\text{K}^{-1})^2 = 95.23 + 1432.3V_{\text{Ni}} + 1257V_{\text{Ni}}^2$. Experimental data agree closely with the predictions of eq. (7).

Finally, an expression of the thermal conductivity of porous Ni/YSZ cermets as a function of composition and porosity is derived from eqs. (6) and (7) as follows:

$$\lambda_c = \frac{1}{8} \{K_A + (K_A^2 + K_B)^{1/2}\} (1-P)(2-3P), \quad \left(0 \leq P < \frac{2}{3}\right). \quad (8)$$

The relationship between all measured data and the calculations from eq. (8) for 1273 K is shown in Fig. 9. All data points fall close to the line with an inclination of

Fig. 8 Comparison of the experimental thermal conductivity (λ_s) of the solid phase with the predictions by Eucken's, Russell's, and Franci-Kingery's equations and by the modified effective medium theory for 1273 K. The measured values are adopted in the case of $V_{\text{Ni}}=0.00$ and $V_{\text{Ni}}=1.00$. Except for these the estimated values obtained by extrapolation to porosity=0 in the curve for eq. (6).

Fig. 9 Comparison of the measured thermal conductivity of porous Ni/YSZ cermets with the prediction calculated by eq. (7) based on the modified effective-medium theory for 1273 K. The numbers close to marks correspond to the sample numbers in Table 1.

unity under a wide range of porosities from 0 to 0.54 and of Ni-volume fractions from 0 to 1. Therefore, the effectiveness of eq. (8) is confirmed as an expression of the thermal conductivity of porous Ni/YSZ cermets at high temperatures.

V. Conclusions

The temperature dependence of the specific heat and thermal conductivity of Ni/YSZ cermets is positive but small in change within 3% at temperatures of 1073 to 1273 K. That of the thermal diffusivity, however, cannot be observed. The specific heat is independent of porosity and is governed by the law of mixing in composition. An abrupt fall in thermal diffusivity was observed when increasing the porosity. Pores in the cermet acted as heat barriers to prevent any heat transfer in which thermal conductivity was regarded as zero. The thermal conductivity can be expressed by the resultant conductivity of a simple cubic-resistor network randomly composed of three kinds of unit resistors corresponding to Ni, YSZ, and pore phases based on the modified effective medium theory.

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