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THERMAL CONDUCTIVITY OF SINGLE- AND MULTI-PHASE COMPOSITIONS IN THE $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ SYSTEM

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ABSTRACT

Compositions in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system are of interest as low thermal conductivity, fracture resistant oxides for the next generation thermal barrier coatings (TBC). Multiple phases occur in the system offering the opportunity to compare the thermal properties of single, two-phase, and three-phase materials. Despite rather large variations in compositions almost all the solid solution compounds had rather similar thermal conductivities and, furthermore, exhibited only relatively small variations with temperature up to 1000°C. These characteristics are attributed to the extensive mass disorder in all the compounds and, in turn, small interfacial Kapitza (thermal) resistances. More complicated behavior, associated with the transformation from the tetragonal to monoclinic phase, occurs on long-term annealing in air of some of the compositions. However, the phases in two of the compositional regions do not change with annealing in air and their thermal conductivities remain unchanged suggesting they may be suitable for further exploration as thermally stable TBC overcoats.

Keywords: thermal conductivity, thermal barrier coatings, mass disorder, phase transformation, Kapitza resistance

1 INTRODUCTION

There is currently an on-going world-wide quest for thermal barrier coating materials capable of higher temperature operation than the state-of-the-art oxide based on $\text{ZrO}_2\text{-7wt.\%Y}_2\text{O}_3$ (7YSZ) [1, 2]. Although many oxides have low thermal conductivity, in several instances even lower than 7YSZ [3, 4], they lack the requisite fracture toughness needed to resist delamination and impact. The task is complex because of the stringent requirements of a TBC, a combination of low thermal conductivity at high temperature, compatibility with alumina as well as high fracture toughness [5]. Previous studies have identified the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system as particularly promising, especially tetragonal compositions lying along the $\text{ZrO}_2\text{-YTaO}_4$ join, a narrow compositional range formed by equi-molar tri-valent and penta-valent additions [3, 6]. In particular, these compositions are phase stable at 1500°C and particularly resistant to sulfate/vanadate corrosion [7]. Moreover, they exhibit very high levels of tetragonality which results in indentation fracture toughness values comparable or higher than 7YSZ [8, 9]. Furthermore, both Raghavan [6] and Shen et al. [10] have demonstrated that compositions along the $\text{ZrO}_2\text{-YTaO}_4$ join have especially low thermal conductivity provided the transformation to monoclinic zirconia is prevented from occurring. The low thermal conductivities are attributed to the extensive mass disorder associated with compositions along the join. They are also resistant to moisture-induced low-temperature transformation [11].

The purpose of this work was to investigate the thermal conductivity over a broader range of compositions in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system and compare the behavior of single and multi-phase oxides. The compositions investigated are shown superimposed on the phase diagram in Figure 1. They include two single-phase solid solutions (the 7YSZ baseline and 16Y16Ta), two compounds (YTaO_4 and $\delta\text{-Zr}_3\text{Y}_4\text{O}_{12}$), a pair of two-phase materials (22Y13Ta and 20Y20Ta) and one comprising three phases (18Y28Ta). The ternary compositions were selected to encompass the non-transformable tetragonal phase as one of the constituents, with the expectation that this would provide a toughness benefit based on prior work [8]. Materials having compositions lying in the two-phase field between the co-doped tetragonal ZrO_2 and the orthorhombic 'O' phase were found to partially transform on cooling and consequently, they were not studied further. Also shown in Figure 1 are compositions whose thermal conductivities have been

reported elsewhere [10, 12, 13]. Compositions within the fluorite single-phase field were also not explored since their thermal conductivities have already been reasonably well studied [14] and were found earlier to have lower fracture toughness [15].

2 EXPERIMENTAL METHODS

The experimental procedures were chosen to produce chemically-homogeneous, fully-dense materials so that the intrinsic thermal conductivities could be measured without needing to apply corrections for the presence and shape of any porosity. In the few cases that the materials could not be made fully dense, particularly for YTaO_4 composition, correction factors were applied with the assumption of spherical pores. Samples were prepared by both current assisted densification process (CADPro) [16] and conventional sintering. The latter process yielded micron-sized grains whereas the former produced nano-scale grains, which enabled the study of the effect of grain size on thermal conductivity upon aging at prospective use temperatures.

2.1 Synthesis of powders

Powders were synthesized by a reverse co-precipitation method [17] in which yttrium nitrate and zirconium oxychloride aqueous solutions were mixed with tantalum chloride solutions in ethanol and then precipitated in ammonium hydroxide [15]. The resulting precipitates were separated from the solvents by centrifugation, repeatedly washed in water and ethanol before drying and then calcined in air at 950°C for four hours. These powders were then cold-pressed and sintered at 1500°C in air for 35-40 h to form a dense pellet.

2.2 Densification and Annealing

For samples prepared by sintering, the powders were cold-pressed (300 MPa) and heat treated at 1500°C in air for 20 h to form dense pellets. For CADPro specimens, the powders were loaded into a graphite die and were simultaneously pressed (130MPa) and heated (at $100^\circ\text{C}/\text{min}$) to 1150°C for 10 to 15 minutes in vacuum (6.7 Pa), and then quickly cooled to room temperature. To restore the oxygen stoichiometry after densification in the reducing atmosphere of the CADPro chamber the samples were subsequently heat treated in air at 900°C for 4 h. Specimens

were characterized using methods described in the following subsections after annealing times of 1, 10, 50 and 100 h at 1200°C in air.

2.3 Thermal property measurement

For thermal diffusivity (α) measurements, specimens were coated with gold and then graphite on both sides. The measurements were conducted in flowing argon gas with a laser flash instrument (Micro Flash® LFA 457, Netzsch, Selb, Germany), from room temperature to 1000 °C. The thermal conductivity (κ) was obtained from the standard relationship,

$$\kappa = \alpha \cdot \rho \cdot C_p \quad (1)$$

where C_p is the heat capacity obtained from calculation using the Kopp-Neumann rule [18] from literature data of pure zirconia, yttria, and tantala, and ρ is the mass density measured using Archimedes method.

2.4. Phase and Microstructural Characterization

The phase contents of the samples were analyzed by X-ray diffraction (D8 Bruker, Karlsruhe, Germany) and Raman spectroscopy (LabRAM Aramis, Horiba – Jobin Yvon, Edison, NJ). Grain size was measured from SEM images (Ultra, Zeiss, Germany) of sintered surfaces and fracture surfaces using a linear-intercept method.

3 RESULTS

The microstructures of the conventionally sintered samples and the CADPro samples after 100 h annealing are shown in Figures 2. They clearly demonstrate the considerably smaller grain sizes of the materials produced by CADPro, even after 100 h annealing at 1200°C. The phases present after densification were consistent with the reported phase diagram at 1500°C, shown in Figure 1, although as will be described later some of the phases transform on prolonged aging at 1200°C. These are illustrated in the X-ray diffraction patterns, Figure 3. The peaks in the diffraction patterns recorded from the samples immediately after CADPro densification were broader due to the small grain size and the peaks subsequently narrowed with prolonged heat treatment. The patterns recorded after different annealing times indicated, though, that the

phases were unchanged with the exception of the solid solution 16Y16Ta and the two-phase 20Y20Ta, which slowly transformed to monoclinic zirconia and a zirconia containing YTaO_4 monoclinic solid solution. The formation of monoclinic zirconia in the 16Y16Ta and 20Y20Ta materials is shown most clearly by the appearance of the characteristic monoclinic lines (arrowed) in the Raman spectra reproduced in Figure 4. Interestingly, samples of the same two compositions prepared by conventional sintering for at least 4 h but at the higher temperature 1500°C did not undergo the same transformation as the CADPro samples annealed at 1200°C .

The thermal conductivities of the single phase, two-phase and three-phase materials, prepared by CADPro, as a function of temperature are shown in Figure 5 together with data for other single phase, polycrystalline phases in the system prepared as part of this work. Figure 5(a) compares the thermal conductivities with those of dense 7YSZ, the orthorhombic phase, the delta phase and the pure YTaO_4 phases. The evolution of thermal conductivity with aging is also shown in Figure 5 together with the data for the larger grain sintered materials. Consistent with the phase evolution upon aging, the conductivities of the compositions whose phases remain stable do not change appreciably whereas those that do transform change, with an initial increase followed by a steady decrease with aging time. Despite these variations, the thermal conductivities of all the materials are largely independent of temperature with the exception of those two in which partial transformation to monoclinic occurred on aging at 50 h and line compound YTaO_4 .

4. DISCUSSION

The most striking feature of the results presented in this work is that the thermal conductivities of all but the compounds lying along the edges of the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ phase diagram are almost independent of composition and are also independent of temperature above room temperature (Figure 5). As will be described, both of these characteristics are related and can qualitatively be understood as being a consequence of the large mean atomic mass of the compounds and the extensive site disorder possible resulting from different atomic arrangements of the individual ions on equivalent crystallographic sites within the crystal structures of the phases involved. Less

obvious is the finding that there is little difference between the thermal conductivities of the single phase, two-phase and three-phase compositions. These findings will be discussed in the following sub-sections in terms of the Klemens-Callaway phonon scattering model [19, 20] which relates the thermal conductivity, κ_i , to temperature, T , and the concentration of randomly distributed point defects through the phonon scattering term, Γ , introduced in the following sub-section:

$$\kappa_i = \kappa_{\min} + \frac{k_B \sqrt{v_s}}{\sqrt{\pi^3} \sqrt{\Omega_0 \Gamma}} \frac{1}{\sqrt{C}} \frac{1}{\sqrt{T}} \tan^{-1} \left(\frac{k_B T_D}{\hbar} \left(\frac{\Omega_0 \Gamma}{4\pi v_s^3 C T} \right)^{1/2} \right) \quad (2)$$

where C describes anharmonic phonon-phonon scattering in the pure, defect-free compound and is independent of defect concentration, v_s is the acoustic velocity, T_D is the Debye temperature, Ω_0 is the unit cell volume, and k_B and $\hbar$ are the Boltzmann and Planck constants, respectively. The first term expresses the minimum value of the thermal conductivity at high temperatures and is temperature independent. It has the same form as first derived by Roufosse and Klemens [21] and notably is independent of the defect concentration. Its value is related to the minimum inter-atomic distance and the mass of the compound, and can be expressed as [3, 22]

$$\kappa_{\min} = 0.87 k_B \left(\frac{n \rho N_A}{\bar{M}} \right)^{2/3} \left(\frac{E}{\rho} \right)^{1/2} \quad (3)$$

where $\bar{M}$ and n are the mean atomic mass and the number of the ions in the unit cell, respectively, E is Young's modulus, ρ is the density and N_A is Avogadro's number. The second term in equation 2 is the conductivity derived by Callaway-von Baeyer [20] and is identical to their equation 23.

4.1. Similarity of thermal conductivities

In contrast with the pure oxides and stoichiometric YTaO₄, in which there is no significant site disorder, each composition in the ZrO₂-Y₂O₃-Ta₂O₅ ternary (Figure 1) is either a solid solution or a mixture of two or more solid solution phases. This has two important implications. The first is that there can be local mass variations due to a heavier or lighter atom substituting for the atom that usually occupies a particular crystallographic site. For example, as Y and Ta are added in equal amounts to ZrO₂, they substitute onto the Zr-site producing spatial variations in atomic mass throughout the solid solution. A vacancy is an extreme case of such a mass variation but other variations in the ternary solid solution are also associated with Y³⁺ and /or Ta⁵⁺ ions substituting on a Zr⁴⁺ site. Along the ZrO₂-YTaO₄ line, no structural vacancies are required for charge neutrality but for all other compositions inside the ternary phase field, either oxygen or cation vacancies will form to maintain charge neutrality. The second implication, discussed in section 4.3 below, is that the interfaces between the phases and grains may lower the thermal conductivities.

According to the Klemens-Callaway model above, phonon scattering is proportional to the product of the variances in atomic mass at each crystallographic site and their concentrations. Specifically, if each solid solution compound contains p distinct crystallographic sub-lattice sites and several different ions, j , can occupy each of these sites, the mass disorder is related to the concentration of the different ions on each crystallographic site and the scattering cross-section is given by the expression [23], [24], [25]:

$$\Gamma = \sum_{i=1}^p \frac{n_i}{n} \left(\frac{M_i}{\overline{M}} \right)^2 \Gamma_i = \sum_{i=1}^p \frac{n_i}{n} \left(\frac{\overline{M}_i}{\overline{M}} \right)^2 \frac{\sum_j f_j (M_j - \overline{M}_i)^2}{(\overline{M}_i)^2} \quad (4)$$

where n is the total number of atoms in the unit cell, n_i is the number of atoms on the sub-lattice, i , $\overline{M}$ is the mean mass of the unit cell, $\overline{M}_i$ is the mean mass on the i -th sub-lattice and Γ_i is the phonon scattering coefficient from mass variance on the i -th sub-lattice. The variance of the masses on each sub-lattice, in effect the “mass disorder”, $(\Delta M_i)^2 = (M_j - \overline{M}_i)^2$ in equation

4, is weighted by their fractional concentrations, f_j . For example, for the 16Y16Ta solid solution composition, the fractional concentrations of Zr, Y and Ta ions on the cation sublattice would be 0.68, 0.16 and 0.16, respectively.

In addition to the effects of phonon scattering from point defects, the thermal conductivity also scales as the inverse square root of the mean atomic mass of the compound [26]. (This dependency is embedded in the phonon-phonon scattering parameter, C , in equation 2). Since the atomic masses of Y and Zr are almost the same and are both only approximately half of that of Ta, there is a tendency for the thermal conductivity to also decrease as the concentration of Ta increases.

4.2 Temperature independence of thermal conductivity

The small variation of conductivity with temperature exhibited by all the compositions is in marked contrast to the temperature dependence of the thermal conductivity of relatively defect-free oxides, such as sapphire and MgO [27]. In such oxides, the conductivity varies with the inverse of temperature approaching a temperature-independent value associated with the minimum thermal conductivity at very high temperatures, typically several times the Debye temperature. Until recently, measurements were either not made over a sufficiently large temperature range to detect significant variations from the $1/T$ dependence or the increasing contribution from radiative heat transfer with temperature masked the higher-temperature behavior arising from phonon scattering.

As is evident from the form of the Klemens-Callaway model (equations 2), mass variations decrease the temperature variation of the thermal conductivity. This is illustrated by the calculations shown in Figure 6 in which the thermal conductivity is plotted against temperature for various defect phonon scattering strengths using YSZ as an example since the other parameters in equation 2 are known for this oxide (taken from Limarga et al. [28]). At low scattering strengths ($\Gamma \rightarrow 0$), the second term in equation 2 asymptotes to an inverse dependence of temperature, the perfect, defect-free crystal limit, given by:

$$\kappa_i = \kappa_{\min} + \frac{k_B^2 T_D}{2\pi^2 v_s \hbar C T} \quad (5)$$

In contrast, as the scattering strength increases, the contribution of the second term becomes increasingly smaller until there is no longer any temperature dependence above the Debye temperature and the thermal conductivity approaches the value of $\kappa_{\min}$, as illustrated in Figure 6). This is consistent with the conductivity data in Figure 5, showing little dependence on temperature above room temperature, with the exception of a weak dependence for the 7YSZ and YTao_4 . Thus, one can conclude that in the compositional fields studied, there is sufficient mass disorder (large Γ) in each of the compounds that their conductivities are close to their minimum thermal conductivities. As these can be expected to be rather similar, little variation of conductivity with composition within a single phase occurs.

4.3. Thermal conductivity in multiple phase compositions

The observations that there is little difference in the thermal conductivity between single phase and multiple phase compositions require explanation. This is especially so when there are several reported instances of significant changes in thermal conductivity in two-phase composites with volume fraction of the two phases, most notably in SiC/Al [29] and diamond/ZnS composites [30, 31]. Although there is no detailed model for phonon scattering in multiple phase materials, one would expect that there would be two contributions to the thermal conductivity. The first would be a volume fraction effect that weights the fraction of the macroscopic thermal conductivity of each phase according to their shapes and orientations. The second would be an effect due to the phonon scattering at the interfaces between dissimilar phases that incorporates both the crystallographic mis-orientation, the origin of the grain size effect on thermal conductivity in polycrystalline materials, and the differential acoustic scattering due to the two phases. The acoustic mismatch interface model [32] accounts for scattering due to differences in the acoustic properties across a planar interface but not specifically other effects. However, macroscopically, these effects can be described by effective medium computations that incorporate an effective grain boundary resistance, a Kapitza resistance, R_k , in series with the grains. A general formulation that takes into account the shapes and orientations of the phases as well their volume fractions and thermal conductivities has been developed by Nan et al.[33].

For the particular case of a two-phase material consisting of spherical particles in a matrix phase with an interface thermal resistance between them the expression for the thermal conductivity reduces to the simple form:

$$\kappa^* = \kappa_m \frac{(1 + 2\alpha) + 2\kappa_r + 2f_v [(1 - \alpha) - \kappa_r]}{(1 + 2\alpha) + 2\kappa_r - f_v [(1 - \alpha) - \kappa_r]} \quad (5)$$

where the second phase, the “particle”, is embedded in major phase of conductivity, κ_m , and the parameter κ_r is the ratio of the thermal conductivities of the two phases, κ_m/κ_p , and f_v is the volume fraction of the second phase particle. The non-dimensional parameter, α , is the ratio of two characteristic lengths, the interface thermal width, $R_k \kappa_m$ and the second phase particle radius, a :

$$\alpha = \frac{R_k \kappa_m}{a} \quad (6)$$

There are two extremes of equation 5 with interface resistance. In the limit, $\alpha \rightarrow 0$ the interface has zero thermal resistance. Then, the thermal conductivity of the two-phase materials simply lies between the arithmetic and the harmonic means of the volume fraction weighted conductivity and the equation reduces to the well-known relationship for the conductivity of randomly distributed particulate composites [34]. When the interfaces have very large thermal resistance, the thermal conductivity approaches a constant value of $2(1 - f_v)\kappa_m / (2 + f_v)$, independent of the thermal conductivity ratio. In between, where interfaces have finite thermal resistances, then examination of equations 5 and 6 indicates that unless the thermal conductivities of the constituent phases are very different, the composite’s thermal conductivity is again almost independent of the interface resistance unless the grain size is only a few nanometers. This is illustrated by the calculations shown in Figure 6(b) in which the thermal conductivity, normalized by the conductivity of the “matrix” conductivity, is plotted as a function of the Kapitza resistance for different volume fractions of the “particle” phase. The Kapitza resistance is not known for any of the compounds investigated in this work but values of 4.5×10^{-7}

$9 \text{ m}^2\text{K/W}$ and $4.0 \times 10^{-9} \text{ m}^2\text{K/W}$ have been reported for the grain boundaries in other oxides, 7YSZ [28] and SrTiO_3 [35], respectively. Recent measurements of grain boundaries in twist bi-crystals of alumina, while showing some small angular dependence, are somewhat higher but similar, $\sim 10 \times 10^{-9} \text{ m}^2\text{K/W}$ [36]. Taking these values as representative and the grain size of the order of 0.1 microns (Figure 2), the value of α is equal to 0.1 for the cases where the thermal conductivity of the matrix phase is 1.5 W/mK and the particle conductivity is 2 W/mK . Consequently, we can conclude that because the thermal conductivities of each of the phases are small, similar, and relatively independent of composition, the thermal conductivities of the multiple-phase compositions investigated are only weakly dependent on the interface resistance, the variation being about $\pm 10\%$.

In the multiphase regions, the constituent solid solution phases (indicated by the appropriate tie lines) have similar mass disorder, meaning that the thermal conductivities are quite similar. For example, the 22Y13T composition consists of two phases, approximately 17Y17Ta and 25Y10Ta, which have mass scattering coefficients of 0.08 and 0.13, respectively, and similar thermal conductivities (at around $1.5 - 1.6$ at 1000°C). As a result, the thermal conductivity of the two phase mixture is only slightly lower than the single solid solution phases, with most of the difference originating from the increase in the grain interface because of small grain size.

At the microscopic, phonon scattering level, the insensitivity to the phase content within the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ ternary system is primarily due to the extremely short phonon mean free paths in the individual phases. A consequence of this is that the presence of interfaces cannot be expected to reduce the already small phonon mean free path further and so the conductivity cannot be significantly reduced. Similarly, the same arguments provide a qualitative explanation for why the three-phase materials also exhibit low and temperature independent conductivities.

4.4. Grain size effects on thermal conductivity.

The comparison between the thermal conductivities, in Figure 5, measured after different annealing times at 1200°C as well as the comparison with the measurements made on sintered samples suggests that there is possibly a small effect of grain size for the three phase composition

and 7YSZ but none in the others. (The grain size effect on the conductivity of 7YSZ has been reported previously [28]). More significant is the reduction in conductivity in the 16Y16Ta and 20Y20Ta on aging associated with the occurrence of micro-cracking due to the de-stabilization of tetragonal zirconia and the formation of monoclinic zirconia. In some cases, such as after 100 h at 1200°C, distinct, macroscopic cracks were observable but in all cases, there is a direct correlation between the reduction in thermal conductivity on annealing and the volume fraction of monoclinic zirconia. Another characteristic of transformation-induced microcracked materials is that the room temperature conductivities are unchanged, presumably because the microcracks close up on cooling, but exhibit reduced conductivities at higher temperatures, due to the transformation opening up the microcracks.

4.5. Interpolations to other compositions.

While the compositions we selected for measurement were chosen to provide information on the thermal conductivity in different regions of the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ phase diagram, it is of interest to estimate the conductivities of other compositions in the same system. As described in the appendix, these conductivities can be obtained by an interpolation scheme based on the models discussed in the previous sub-sections using the measurements presented in this work together with the reported conductivities of pure ZrO_2 [6] and Y_2O_3 [37]. The results of these interpolations are plotted in Figure 6(c) and (d) and show only small variations in thermal conductivity with composition except close to pure ZrO_2 , Y_2O_3 , and Ta_2O_5 , particularly at 1000°C.

5. CONCLUDING REMARKS

The thermal conductivity of materials with various compositions within the zirconia-rich portion of the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ phase diagram are all low (<1.7 W/mK), significantly lower than 7YSZ and also exhibit only a weak dependence on temperature from room temperature to 1000°C, unlike simple oxides such as alumina, MgO, ZrO_2 , and Y_2O_3 . The relative insensitivity to composition and phase content is attributed to three factors. One is the small phonon mean free paths produced by extensive mass disorder within each of the crystalline phases associated with large ranges of solubility of ions of different masses. The second factor, which is related, is that the small mean free paths are close to the minimum associated with the minimum thermal

conductivity. The third is that for the grain sizes investigated, greater than about 0.2 micron, the effect of the thermal resistance of grain and inter-phase boundaries is relatively small meaning that the conductivity is relatively insensitive to the grain size of the phases.

One of the consequences of our findings and analysis is that if compositions in the $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{-Ta}_2\text{O}_5$ field are used as thermal barrier coatings, controlling their composition will not be important, at least as far as the thermal conductivity is concerned.

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