**NANOSTRUCTURED MATERIALS FOR MICROSTRUCTURAL
CONTROL OF THERMAL PROPERTIES***

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August 2000

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Invited paper submitted to the proceedings of the NATO Advanced Study Institute on "Functional Gradient Materials and Surface Layers Prepared by Fine Particle Technology", Kiev, Ukraine held on June 18-28, 2000.

*Work supported by the U.S. Department of Energy, Office of Science under Contract W-31-109-ENG-38.

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1. Introduction

Compared to many other properties of nanostructured materials such as their mechanical behavior, thermal transport properties have received considerably less attention. Recently, however, this area has begun to attract attention. It is well known that conventional polycrystalline materials typically exhibit lower thermal conductivity than low-defect single crystals of the same material. Several investigators have realized recently that this could result in significantly reduced thermal conductivities in nanostructured materials that could lead to important improvements in behavior for applications such as thermal barrier coatings (TBC's). Recent studies of grain-size-dependent thermal conductivity in yttria-stabilized zirconia (YSZ), the most commonly utilized thermal barrier material, have begun to investigate the feasibility of using nanostructured components in future-generation TBC's [2-4].

While a grain-size-dependent reduction in thermal conductivity may be desirable for thermal barrier applications, there are other applications involving nanometer-scale microstructures where retention of high heat transfer rates is desirable. For example, the continual trend towards miniaturization in the micro-electronics industry is resulting in

increased localization of heat loads with concomitant increasing thermal management challenges. Cooling systems based on fluids pumped through heat exchangers become unfeasible when component sizes are reduced to the nanometer scale. The development of new solid-state high thermal conductivity "heat pipes" synthesized, for example, from thin film diamond nanostructures would provide important advantages if the nanostructure processing can be optimized to maintain sufficient heat transport rates.

The role of microstructure in controlling heat transfer properties in nanostructured materials will be discussed in this paper, with emphasis on discussing the possible effects of grain size in controlling conductive heat transfer via changes in sound velocity, specific heat, or phonon mean-free-path.

2. Heat Transport Fundamentals

There are two fundamental mechanisms of heat transfer in materials [5]: 1) radiative heat transfer, which is transfer of heat by photon emission, and 2) conductive heat transfer, which is transfer of heat by molecular or atomic motion. Convection is sometimes considered a third heat transfer mechanism, but more appropriately should be considered to be simply correlated conductive heat transfer [5].

Radiative heat transfer is particularly important at high temperatures, such as may be encountered in TBC applications. A detailed study of the effects of grain size, if any, on radiative heat transfer at high temperatures has not been carried out to-date, however, and thus this mechanism will not be discussed further in this brief review. At room temperature or below, where limited studies of grain size effects on thermal conductivity have been performed (e.g., [4, 6]), contributions from radiative heat transfer are expected to be negligible.

There are three mechanisms of conductive heat transfer. Uncorrelated molecular collisions transfer heat via a ballistic process. Ballistic heat transfer is dominant in non-crystalline materials, including liquids, gases, and amorphous solids. Heat transfer by correlated atomic motion (phonons) occurs in all crystalline solids. In electrical conductors, significant heat transfer also occurs through the motion of conduction

electrons. The focus here is on heat transfer in materials where electron motion contributions to the thermal transport properties are negligible, however, such as for materials including yttria-stabilized zirconia (YSZ) and diamond.

3. Expected Effects of Grain Size on Thermal Conductivity

For situations where the number of phonon scattering events is large and random, as is the case in nanostructured materials with randomly oriented and spaced grain boundaries, a particle transport approach is appropriate for understanding heat transfer via phonons (as opposed to an approach taking into account the wavelike nature of the phonons, which may be more appropriate in other cases). A kinetic theory approach based on particle-based energy transport can be used to derive a simple relationship between thermal conductivity, k , specific heat, C , sound velocity, v , and phonon mean-free-path, l [7]:

$$k = \frac{Cvl}{3} \quad (1)$$

By examining the potential grain size effect on each of the quantities in the numerator of the right-hand-side of Eq. 1 it should be possible to predict a relationship between grain size and thermal conductivity for nanostructured materials.

Reports in the literature to-date indicate little or no effect of grain size on specific heat in nanocrystalline materials. Lu et al. [8] observed that for measurements from ~300-500K, nanocrystalline Ni-P alloys exhibited approximately 10% larger specific heat values than either amorphous or coarse-grained polycrystalline alloys of the same composition. In the case of diamond, Moelle et al. [9] found that for temperatures of approximately 50-300°C, no measurable differences were observed between the specific heats of single crystal, coarse-grained polycrystalline, and nanocrystalline diamond samples. Based on these reports, it is expected that changes in specific heat will have little contribution to any grain-size-dependent changes in thermal conductivity.

To the best of our knowledge, at the present time there are no reported direct measurements of sound velocity as a function of grain size in nanocrystalline materials. Since v is related to the bulk modulus, B , and the density, ρ , according to

$$v = \left(\frac{B}{\rho} \right)^{1/2} \quad (2)$$

grain-size-dependent changes in either B or ρ could affect v . Reduced elastic moduli compared to bulk values have been reported for both nanocrystalline ceramics [10] and metals [11]. However, this reduction has generally been interpreted as resulting from porosity due to sample processing rather than being an intrinsic grain-size effect. While it is possible that a real reduction in moduli could occur in extremely fine-grained nanocrystalline materials, this would be expected to occur simultaneously with a lower expected density in grain boundary regions; thus, the net effect of grain size on v is still expected to be negligible.

In contrast to the expectations of minimal effects of grain size on specific heat and sound velocity, grain size is expected to have a significant effect on the phonon mean-free-path, l . Debye [5] derived the relationship

$$l = \frac{20dT_m}{\gamma^2 T} \quad (3)$$

where T_m is the absolute melting temperature, d is the lattice constant, and γ is the Gruneisen constant, which is ~ 2 for most materials [5] and is given by [12]

$$\gamma = \frac{3\alpha B}{C} \quad (4)$$

where α is the thermal expansion coefficient. Particularly at low temperatures, the single crystal l value can be very large compared to nanocrystalline grain sizes. For

example, for single crystal diamond at 10K, $l \approx 1$ mm [6]. For samples with very low defect concentrations, this can lead to a sample-size dependence of k , such as has been observed at low temperatures in LiF [13].

Due to scattering of phonons by grain boundaries, reducing the grain size below the calculated single-crystal l value should result in a reduced phonon mean-free-path and consequently a reduction in k . Based on this type of argument, theoretical predictions have been made of grain-size-dependent reductions in k in nanocrystalline materials such as YSZ [2]. A lower limit can be predicted for k by substituting the interatomic spacing for l in Eq. 1 [14]. A wide range of amorphous and highly defective crystalline materials have been found to exhibit thermal conductivities well-represented by this minimum thermal conductivity criterion [14-15].

4. Experimental Studies of the Effect of Grain Size on Thermal Conductivity

Relatively few experimental studies of the grain-size-dependence of thermal conductivity have been performed to-date. Results for both nanocrystalline YSZ [3,4] and diamond [6, 16-18] will be briefly reviewed in this section. Since YSZ is highly defective and exhibits low thermal conductivity even in single crystal form due to the large oxygen vacancy concentration required to maintain charge neutrality, the effect of grain size on k is expected to be much smaller than for a material like diamond which can exist as highly perfect single crystals with extremely large thermal conductivity.

4.1 THERMAL CONDUCTIVITY IN NANOCRYSTALLINE YSZ

Raghavan et al. were first to experimentally investigate the thermal conductivity of nanocrystalline YSZ [3]. In that study, bulk samples were prepared from sintered nanocrystalline powders with grain sizes as small as 30 nm. The interpretation of their results was complicated by the significant grain-size-dependent porosity found in all samples with grain sizes less than 70 nm. In particular, they observed no effect of grain

size on thermal conductivity for dense samples, but a significant dependence of the thermal conductivity on varying amounts of porosity for smaller-grained samples.

A more recent study of nanocrystalline YSZ by the present authors and co-workers [4] observed a grain-size-dependent reduction in the room-temperature thermal conductivity of nanocrystalline yttria-stabilized zirconia for the first time. YSZ films with thicknesses of 0.5 - to - 1.2 μm and yttria compositions of 8 to 15 mol.% were grown on polycrystalline $\alpha\text{-Al}_2\text{O}_3$ substrates by metal-organic chemical vapor deposition with controlled grain sizes from 10 to 100 nm. The measured room temperature thermal conductivity values for YSZ thin films as a function of grain size are shown in Figure 1. For all grain sizes larger than 30 nm, the thermal conductivity is approximately constant and ~20% smaller than the literature value of 2.3 W/m-K for

Figure 1. Measured room temperature thermal conductivity values for YSZ thin films as a function of grain size (after [4]). Note that for grain sizes larger than the single crystal phonon mean-free-path, the thermal conductivity is approximately independent of grain size, while for smaller grain sizes a rapid decrease is observed.

high-density, polycrystalline YSZ with a yttria-content of 10 mol.% at 20°C [19]. For smaller grain sizes, the thermal conductivity was observed to decrease rapidly with decreasing grain size, reaching a value of less than one-third the bulk value for the smallest grain-sized samples.

While the measured thermal conductivity values from Ref. [4] are in good agreement with theoretical predictions of Klemens and Gell [2] for grain sizes larger than 30 nm, the observed rapid decrease in thermal conductivity for smaller grain sizes was not predicted. At the smallest grain sizes, the observed thermal conductivity values are approximately half the predicted values for the minimum conductivity amorphous limit of YSZ calculated using an Einstein model [15].

The results of Ref. [4] are in good agreement with Ref. [3] in that both studies found no effect of grain size on thermal conductivity for nanocrystalline YSZ samples with grain sizes larger than ~30 nm. The strong grain-size-dependent effect seen by Soyeux et al. [4] was observed only for samples with significantly smaller grain sizes than measured by Raghavan et al. [3]. From observations that indicated a lack of any systematic change in porosity with changes in grain size, it was concluded in Ref. [4] that the variations in thermal conductivity observed in that study were more likely attributable to changes in grain size than changes in porosity.

A possible explanation for the observed grain size dependence of the thermal conductivity of YSZ in Ref. [4] can be provided by considering the relationship between the grain size of the samples and the phonon mean-free-path. Using Equations 3 and 4, l for single crystal YSZ is calculated to equal 25 nm at 300K. It is reasonable to expect that, consistent with the present observations, reductions in thermal conductivity due to phonon scattering by grain boundaries will only become significant for grain sizes smaller than l . Since l is temperature dependent, this explanation predicts that the critical grain size below which the thermal conductivity drops rapidly compared to the bulk conductivity will also depend on temperature.

4.2 GRAIN-SIZE DEPENDENCE OF THERMAL CONDUCTIVITY IN DIAMOND

At room temperature, the thermal conductivity of high quality single crystals of diamond exceeds 2200 W/m-K [16-18] and can be even larger in isotopically-purified single crystals [20]. Since this is approximately three orders-of-magnitude larger than the thermal conductivity of YSZ, there is a potential for a much larger grain-size effect. Two recent studies have begun to address this issue.

Graebner and co-workers were the first to investigate grain-size dependent thermal conductivity in diamond [16-18]. In those studies, polycrystalline diamond was produced by chemical vapor deposition and the thermal conductivity was measured at room temperature. Their samples were found to exhibit a columnar morphology that resulted in an increasing in-plane grain size with increasing film thickness (distance from the silicon substrate). By examining the thermal conductivity of samples of several thicknesses, the authors were able to infer an effect of grain-size. They concluded that samples with grain sizes larger than approximately 20 μm exhibited essentially single-crystal-like conductivity, while below that grain size the conductivity decreased monotonically to a value of approximately 25% of the single-crystal value for a grain size of about 2 μm . It is interesting and not understood why samples with grain sizes as large as 2-20 μm would show deviations from single crystal thermal conductivity. Using Eq. 1 and literature values for k , C , and ν , l for single crystal diamond would be predicted to be approximately 100 nm at room temperature. The possible role of other microstructural influences were not considered in Ref. [16] (e.g., variations in strain or porosity with changing film thickness).

Efimov and Mezhev-Deglin [6] performed a more recent study of thermal conductivity in diamond films prepared by microwave plasma enhanced chemical vapor deposition. At room temperature, their data indicated no difference in the thermal conductivities of single crystal diamond and a 1-10 μm grain-sized polycrystalline film, but a significantly reduced room temperature thermal conductivity in a 100 nm grain-sized sample. They also obtained data at temperatures as low as 8 K and observed significant reductions in thermal conductivity in both grain-sized polycrystalline samples at low temperatures compared to single crystal diamond. These results seem in

line with expectations based on Eq. 1; however, additional factors such as the presence of an amorphous carbon component in their samples may have influenced the results. Further studies with phase-pure samples are needed to definitively determine the grain-size dependence of thermal conductivity in diamond.

5. Processing of Thin Film Nanostructures by Metal-Organic Chemical Vapor Deposition (MOCVD)

Since nanostructured coatings and films are desirable for potential thermal management applications, processing techniques that provide optimal control of microstructure are needed. Nanocrystalline thin films and coatings have been previously produced by several techniques including thermal spray [21,22], electrodeposition [23], sputter deposition [24], and MOCVD [25,26]. Of these techniques, only thermal spray and MOCVD appear feasible for applications where cost-effectiveness, scalability, and field servicing are major concerns. Previous studies of MOCVD processing of nanocrystalline coatings of TiC, TiN, and SiC [25], and AlN/TiN [26] have established that several strategies can be employed in obtaining and stabilizing nanocrystalline microstructures via MOCVD processing. For example, Liu and co-workers [26] successfully used high speed deposition techniques to suppress relaxation processes believed to result in grain growth. These same workers [26] also established that co-depositing insoluble components to form a composite is an effective means of stabilizing a nanocrystalline microstructure.

Results from a recent study of the processing of nanocrystalline YSZ are described here. Nanocrystalline YSZ films were grown by MOCVD using a low-pressure, horizontal, cold-walled deposition system. Yttrium b-diketonate ($Y(thd)_3$) and zirconium t-butoxide ($Zr(OC(CH_3)_3)_4$) [27] were chosen as precursor materials. High-purity nitrogen was used as the precursor carrier gas. The precursors were mixed with high-purity oxygen and nitrogen in the quartz deposition chamber.

(a)

(b)

Figure 2. Grain size can be controlled by varying MOCVD processing parameters such as (a) the precursor bubbler temperature(s), or (b) the substrate temperature. In (a), the open symbols denote growth rate, while the closed symbols indicate the average grain size.

Figure 3. For nanocrystalline YSZ films grown on polycrystalline alumina substrates x-ray diffraction results indicate that a random texture was observed for all substrate temperatures $< 550^{\circ}\text{C}$ (a), while a strong (100) texture develops for substrate temperatures $\geq 550^{\circ}\text{C}$. The sharp unlabelled peaks in these figures are from the alumina substrate.

A goal in producing a small-grained microstructure is to maximize the nucleation rate. Several process parameters may play a role in accomplishing this, such as the substrate temperature, the bubbler pressures, the carrier gas flow rates, and the bubbler temperatures. For example, increasing the bubbler temperature(s) results in faster growth rates, which suppresses grain growth and decreases grain size, as seen in Fig. 2(a). A difficulty with changing bubbler temperatures in order to control grain size is that, for a multicomponent material such as YSZ, it is difficult to change the grain size without also changing the composition (the temperature dependence of the vapor pressures of the precursor materials typically are different). As a result, a more effective strategy for vary grain size while maintaining approximately constant composition is to hold the bubbler

Figure 4. The effect of annealing on grain growth is shown. YSZ samples grown on polycrystalline alumina substrates were annealed at each temperature for two hours in Ar-0.2% O₂. The heating and cooling rates were 200°C/hr.

temperatures constant while varying the substrate temperature. In this case, while making only small additional changes in the pressure in the Zr precursor bubbler, samples with controlled grain sizes and approximately constant composition can be prepared, as shown in Fig. 2(b). With increasing substrate temperature, the grain size increases smoothly and reproducibly from 10 nm for growth at 500°C to about 100 nm at 600°C, as seen in Fig. 2(b). YSZ samples produced with alumina substrate temperatures < 550°C were found to be non-textured, while a (100) texture was observed to develop at higher growth temperatures as seen in Fig. 3

The resistance of the nanocrystalline microstructure to grain growth at high temperatures is also an important issue when considering potential TBC applications of nanocrystalline YSZ. The onset of rapid grain growth in the YSZ films of the present study was observed to occur at temperatures above approximately 900°C, as seen in Fig. 4. For usage in potential applications above this temperature it will be necessary to develop strategies to suppress grain growth. Co-depositing an insoluble second phase (e.g., alumina) may be one technique for improving the grain size stability.

6. Summary and Conclusions

A review of the possible effects of grain size in phonon-based conductors such as YSZ or diamond indicates that a reduction in phonon mean-free-path below the bulk value is likely to have a significant effect on thermal transport. While the grain size dependences of specific heat and sound velocity have not yet been thoroughly characterized, the expected grain size effects on these quantities is small.

A new type of functional gradient may be desirable for optimizing thermal properties. For example, a grain-size graded YSZ coating could consist of a dense nanometer-grain-sized layer to provide phonon scattering and improved mechanical properties, plus a coarser-grained porous layer that would scatter photons.

Studies of thermal properties in nanostructures comprised of normally high thermal conductivity materials such as diamond have only begun recently and require further

investigation. Process optimization may lead to optimal microstructures that would provide highly localized heat transfer in future microelectronic applications.

This work was supported by the U.S. Department of Energy, Office of Science, under Contract W-31-109-ENG-38.

7. References

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