

NOVEL APPLICATIONS EXPLOITING THE THERMAL  
PROPERTIES OF NANOSTRUCTURED MATERIALS\*

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## NOVEL APPLICATIONS EXPLOITING THE THERMAL PROPERTIES OF NANOSTRUCTURED MATERIALS

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### ABSTRACT

A new class of heat transfer fluids, termed nanofluids, has been developed by suspending nanocrystalline particles in liquids. Due to the orders-of-magnitude larger thermal conductivities of solids compared to those of liquids such as water, significantly enhanced thermal properties are obtained with nanofluids. The use of nanofluids could impact many industrial sectors, including transportation, energy supply and production, electronics, textiles, and paper production by, for example, decreasing pumping power needs or reducing heat exchanger sizes. In contrast to the enhancement in effective thermal transport rates that is obtained when nanoparticles are suspended in fluids, nanocrystalline coatings are expected to exhibit reduced thermal conductivities compared to coarse-grained coatings. Reduced thermal conductivities are predicted to arise because of a reduction in the mean free path of phonons due to presence of grain boundaries. This behavior, combined with improved mechanical properties, makes nanostructured zirconia coatings excellent candidates for future applications as thermal barriers.

## INTRODUCTION

While many properties of nanostructured materials such as mechanical behavior have received considerable attention in the past decade, other properties such as thermal transport have been investigated to a far lesser extent. It is well known that conventional polycrystalline materials 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. Yttria-stabilized zirconia (YSZ) is the typical thermal barrier coating material for applications such as protecting gas turbine components in high temperature environments. While nanocrystalline YSZ has been produced in a few laboratories [1,2] and has been predicted theoretically to have significantly lower thermal conductivity than coarse-grained material [3], the thermal properties have not been explored experimentally. To our knowledge, only a single experimental report of thermal conductivity in nanostructured YSZ exists [4] and this appeared in print less than a month ago. That study was conducted on samples prepared from sintered powders of YSZ and the results were complicated by porosity present in all microstructures with grain sizes below approximately 30 nm. Our approach has been to use metal-organic chemical vapor deposition (MOCVD) processing to produce dense microstructures without elevated temperature sintering. Preliminary results from our new study of nanocrystalline YSZ coatings produced by MOCVD are described below.

Despite considerable previous research and development focusing on industrial heat transfer requirements, major improvements in heat transfer capabilities have been held back because of a fundamental limit in the thermal conductivity of conventional fluids. In contrast to the lowered thermal conductivities expected for bulk 2-D or 3-D nanocrystalline microstructures, we have recently identified an opportunity for increasing the effective thermal conductivities of liquids by dispersing nanometer-sized solid particles into conventional heating and cooling fluids such as water or ethylene glycol (forming what we call nanofluids). The thermal conductivity of heat transfer fluids plays a vital role in the development of energy-efficient heat transfer equipment. Results from our studies of the thermal conductivity and heat transfer coefficient of nanofluids are presented below.

## MICROSTRUCTURE AND PROPERTIES OF NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA COATINGS

YSZ thermal barrier coatings (TBCs) are used in a number of important industrial applications, such as in protecting gas turbine components in high temperature environments. Improved TBC properties are needed for current and future applications, particularly since little progress has been made in recent years in developing new structural alloys that can be used at higher, and thus more efficient, temperatures [5,6]. Turbine component operating temperatures above 1500°C are desired, compared to current typical operating temperatures of 1100°C or below [6]. Improved thermal barrier coatings are believed to provide the best opportunity for attaining the desired higher operating temperatures [5]. Improvements in service lifetimes of components are also desirable and require the development of coatings with improved elevated temperature corrosion resistance, along with improved damage tolerances both at ambient and elevated temperatures. Attaining these goals requires the development of a new class of coatings

with better adhesion properties and high densities, along with improved resistances to thermal transport. We have initiated a program to investigate the thermal and mechanical behavior of nanocrystalline YSZ coatings produced by MOCVD [7].

As seen in the plan-view TEM image shown in Fig. 1 [8], nanocrystalline YSZ coatings can have very small grain sizes. Samples with grain sizes as small as approximately 10 nm and no apparent porosity have been produced on a variety of substrates including single crystal Si and polycrystalline Ni. Coatings on Ni-based superalloys will be grown in the near future.

The excellent process control afforded by MOCVD allows the production of dense coatings with controlled grain size and composition. For example, as seen in Fig. 2, the grain size of  $ZrO_2$  and YSZ coatings can be systematically varied by adjusting parameters such as the substrate temperature. Other process parameters that affect grain size include the metal-organic precursor temperatures and the chamber pressure. For example, we have found that the chamber pressure has a strong effect on grain size. The data shown in Fig. 2 were obtained at a constant chamber pressure of 10 Torr. Reducing this pressure to 5 Torr and maintaining a constant substrate temperature of  $500^\circ C$  results in a reduction in the grain size of YSZ coatings from approximately 30 nm to 10 nm.

The thermal conductivity of coatings can be measured in several ways. We have built a  $3\omega$  system such as that developed by Cahill and co-workers [9] to measure the thermal conductivity of our materials. This technique uses a metal line deposited onto the surface of the coating as both a heater and thermometer. The  $3\omega$  technique is particularly well-suited for measurements of the thermal conductivity of thin films, such as are produced by MOCVD. At present, we have

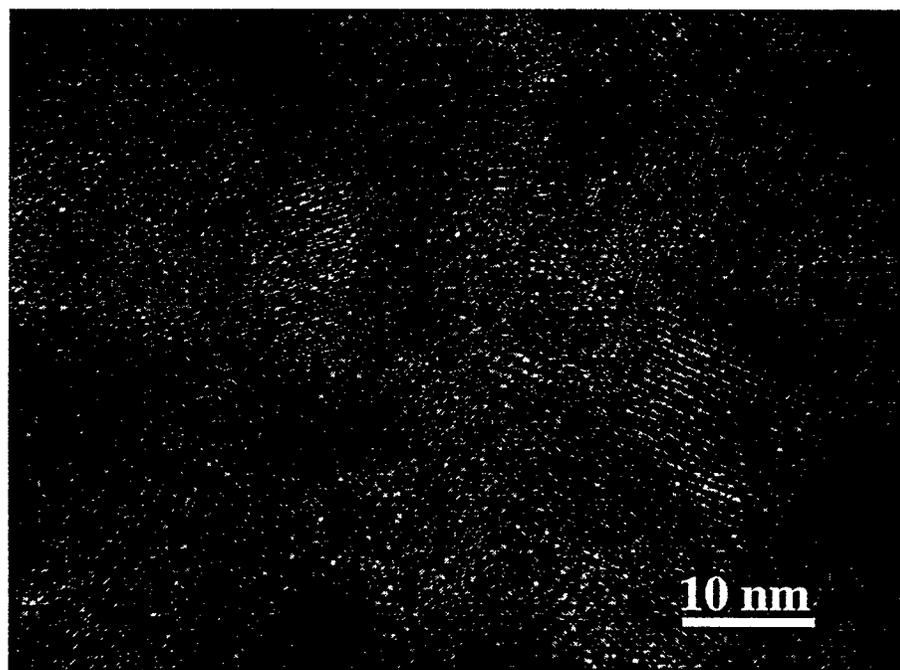


Figure 1. High resolution electron micrograph of a nanocrystalline yttria-stabilized zirconia (YSZ) thin film prepared by MOCVD [8].

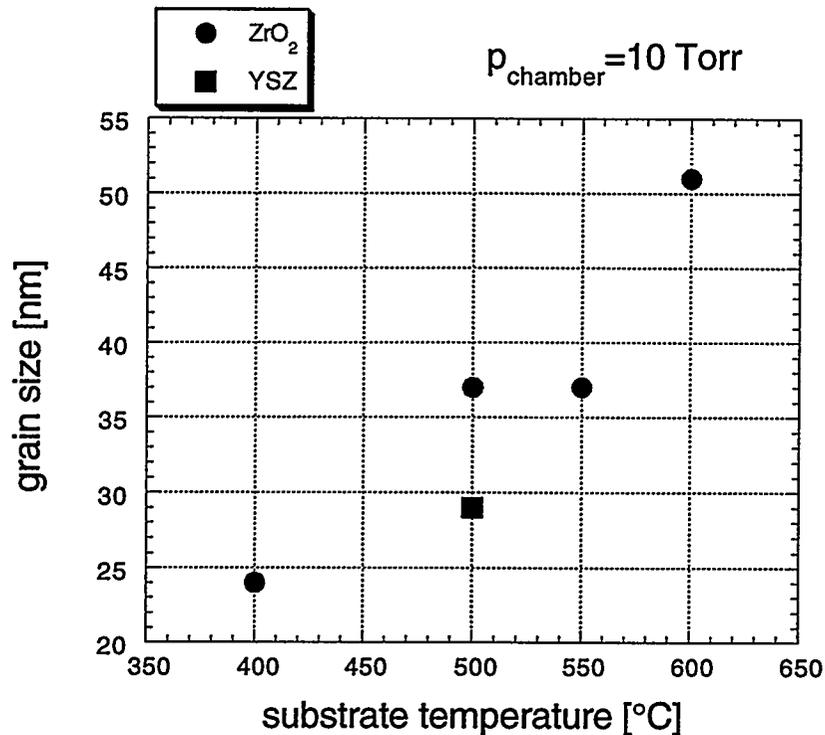


Figure 2. Several MOCVD processing parameters affect grain size. The effect of substrate temperature on grain size at a constant chamber pressure of 10 Torr is shown here for both ZrO<sub>2</sub> and YSZ coatings.

measured the thermal conductivity of single crystal substrates with this apparatus and found reasonable agreement with literature values. Measurements of nanocrystalline YSZ coatings are planned in the near future.

## PROCESSING AND THERMAL PROPERTIES OF NANOFUIDS

It is well known that metals in solid form have thermal conductivities that are higher than those of fluids by orders of magnitude. For example, the thermal conductivity of copper at room temperature is about 700 times greater than that of water and about 3000 times greater than that of engine oil, as shown in Table 1 [10]. Therefore, fluids containing suspended solid metallic particles are expected to display significantly enhanced thermal conductivities relative to those of conventional heat transfer fluids.

Numerous theoretical and experimental studies of the effective thermal conductivity of dispersions containing particles have been conducted since Maxwell's theoretical work [11] was published more than 100 years ago. However, all previous studies of the thermal conductivity of suspensions have been confined to those containing millimeter- or micrometer-sized particles. Maxwell's model shows that the effective thermal conductivity of suspensions containing spherical particles increases with the volume fraction of the solid particles. It is also known that the thermal conductivity of suspensions increases with the ratio of the surface area to volume of the particles.

Table 1. Thermal conductivities of various solids and liquids

Material	Thermal conductivity (W/mK)
Silver	429
Copper	401
Aluminum	237
Silicon	148
Aluminum Oxide	40
Water	0.613
Ethylene Glycol	0.252
Engine Oil	0.145

On the basis of these historical backgrounds and the current synthesizing technique for nanocrystalline particles, it was proposed that nanometer-sized metallic particles can be suspended in industrial heat transfer fluids such as water, ethylene glycol, or engine oil to produce a new class of engineered fluids with high thermal conductivity [12]. Our recent work has demonstrated that nanofluids exhibit significantly enhanced thermal conductivities [13,14] and heat transfer coefficients [15] compared to fluids that do not contain suspended nanoparticles.

Two procedures were used in synthesizing nanofluids for this investigation. In the first, nanocrystalline powders were prepared by the gas condensation (IGC) process and then were subsequently dispersed in deionized water. Nanocrystalline CuO and Al<sub>2</sub>O<sub>3</sub> powders [16] were used in these experiments. Transmission electron microscopy was used to characterize particle sizes and agglomeration behavior.

To successfully produce a nanofluid with dispersed nanocrystalline Cu particles, a second preparation method was used based on the vacuum evaporation onto a running oil substrate (VEROS) technique of Yatsuya et al. [17]. With this technique, nanocrystalline particles are produced by direct evaporation into a low vapor pressure liquid. Low vapor pressures are required with the VEROS technique to prevent vaporization of the liquid during the evaporation process. The system used at Argonne is based on a modification of the VEROS technique and is similar to an earlier design by Günther and co-workers at the Fraunhofer Institute for Applied Materials Research in Bremen [18]. Using this system, nanocrystalline Cu has been evaporated resistively into ethylene glycol. A typical micrograph of nanocrystalline Cu produced by this technique is shown in Fig. 3. Note that the particle size is extremely small (< 10 nm average particle diameter) and there is little particle agglomeration.

Thermal conductivities were measured using a transient hot-wire apparatus described in detail in [13]. Briefly, this system measures the temperature of a wire suspended in a fluid containing controlled concentrations of nanoparticles. The wire is heated resistively and the well-known relationship between the electrical conductivity of the wire and its temperature is used to obtain the temperature-time response of the wire.

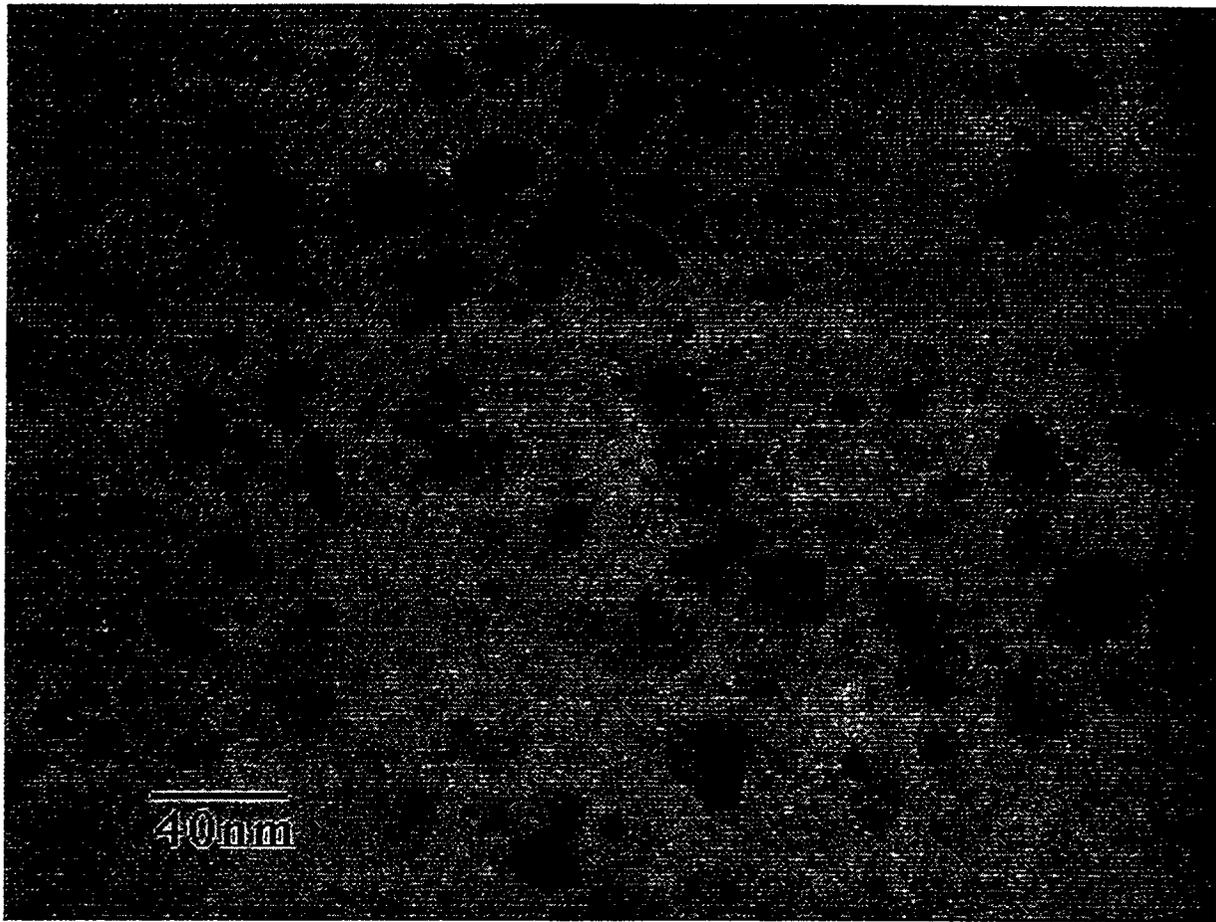


Figure 3. TEM micrograph of nanocrystalline Cu produced by direct evaporation into ethylene glycol.

The thermal conductivities of several nanofluids are shown in Fig. 4 [14]. Thermal conductivity data are plotted normalized to the conductivity of the non-particle-containing fluids. The  $\text{Al}_2\text{O}_3$  and CuO data shown are for nanofluids consisting of nanoparticles dispersed in water, while the Cu data shown are for nanofluids dispersed in ethylene glycol. Significant increases in thermal conductivity are seen for all measured nanofluids compared to the non-particle-containing fluid. The enhancement in thermal conductivity of nanofluids has been shown to depend on the particle size, as well as the thermal conductivity of the particle and fluid materials [14].

In addition to measuring the thermal conductivity of several nanofluids, we have also measured the heat transfer coefficient of nanofluids under dynamic flow conditions [15]. Our data indicate that, at fixed flow rates, a greater than 15% improvement in the heat transfer coefficient of water containing less than 1 vol.% CuO nanoparticles is observed, compared to that of water without nanoparticles. Likewise, these data also indicate that CuO-in-water nanofluids can provide the same rate of heat transfer as pure water at substantially lower flow rates. This in turn would allow the use of smaller and lighter pumps in future applications of nanofluids.

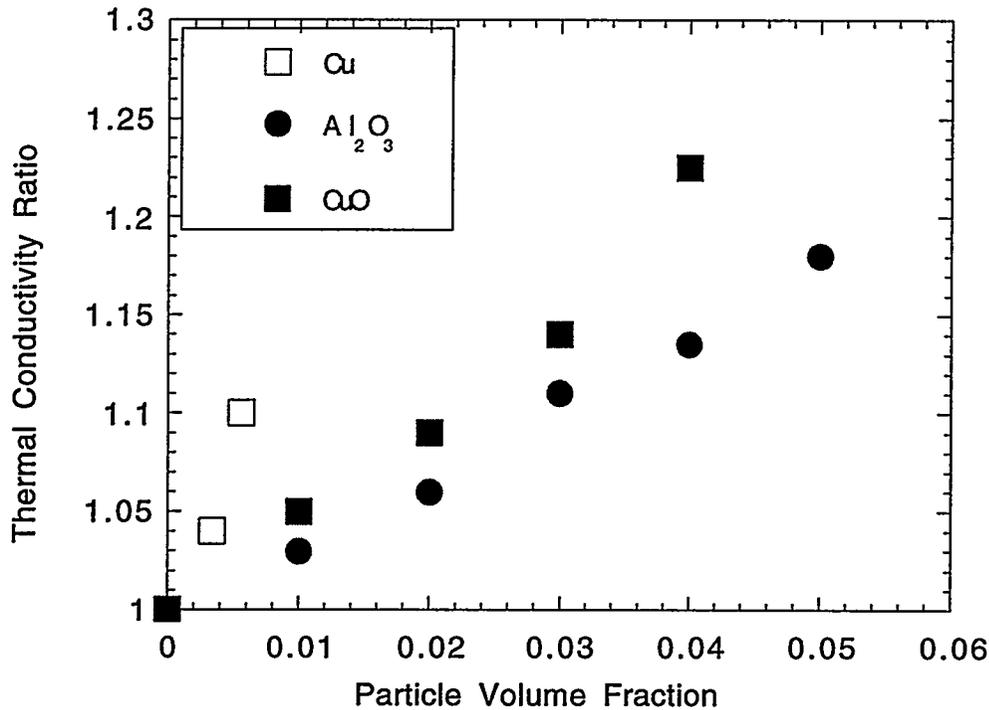


Figure 4. The enhancement in thermal conductivity of three nanofluids is shown. The Cu nanofluid consisted of Cu nanoparticles dispersed in ethylene glycol, while the two sets of oxide data are for nanoparticles dispersed in water.

## FUTURE DIRECTIONS

Much work remains to be done to determine whether nanocrystalline YSZ coatings will provide commercial benefits as thermal barrier coatings. The study of Raghavan et al. [4] found no dependence of the thermal conductivity of YSZ on grain size. However, it is important to note that the phonon mean free path for YSZ calculated using a relationship derived by Debye [19] is on the order of 24 nm at room temperature and drops to only approximately 4 nm at 1800 K. This suggests that microstructures with significantly smaller grain sizes than the  $\geq 30$  nm investigated by Raghavan et al. are required. MOCVD processing has the potential to meet this requirement. A second important consideration is the need to stabilize this nanocrystalline microstructure at the elevated temperatures where a thermal barrier coating would be utilized. One possibility for stabilizing nanocrystalline YSZ to high temperatures is to form composite microstructures, such as YSZ-Al<sub>2</sub>O<sub>3</sub>. Experiments to determine if nanocrystalline YSZ-Al<sub>2</sub>O<sub>3</sub> coatings can be produced by MOCVD are planned in the near future.

There is great industrial interest in nanofluids. Since the appearance of an article on nanofluids in Argonne's "Tech Transfer Highlights" in September 1997, more than 20

companies have contacted Argonne to express interest in nanofluids. These companies include both heat transfer fluid manufacturers and end users. As a further indication of the potential impact of nanofluids technology on industry, the November, 1997 issue of "High-Tech Materials Alert" by John Wiley & Sons, Inc. featured Argonne's nanofluids project on its first page. Also, the October, 1997 issue of "Process Heating" featured nanofluids in its "News Monitor" section. An article on heat transfer fluids including nanofluids appeared in the September 1998 issue of Chemical Engineering magazine. This great industrial interest shows that nanofluids can be considered for a wide variety of industries ranging from transportation, HVAC, energy production and supply, to electronics, textiles, and paper production. All these industries are limited by heat transfer and so have a strong need for improved fluids that can transfer heat more efficiently.

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