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THERMAL SPRAYED NANOSTRUCTURED THERMAL BARRIER COATINGS

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Summary

Nanostructured ceramics exhibit a number of enhanced mechanical and thermal properties which may make them attractive as thermal barrier coatings. The phonon contribution to thermal conductivity is greatly reduced at room temperature, but becomes significant at operating temperatures only for grain sizes below 20 nm. Improvements in mechanical properties, such as fracture toughness and resistance to spalling, can be achieved at larger grain size, in the range of 30 - 70 nm. Suitable coatings, consisting of a composite of zirconia with a second immiscible phase, such as alumina, can be fabricated by thermal spray. However, development of techniques to produce the required microstructure are at an early stage and may require advances in the state of the art for thermal spray technology.

Introduction

Nanostructured materials have traditionally been defined as any material having some physical length scale smaller than 100 nm. This could be a particle size, layer thickness, fiber diameter, or grain size (0-, 1-, 2-, and 3-dimension respectively). The choice of 100 nm is somewhat arbitrary, but is based on the fact that the characteristic length of many interesting mechanical, optical, and magnetic phenomena are of this order. Thus, as the layer thickness or grain size become very small, the associated properties begin to diverge radically from "conventional" values. Another reason why nanostructured materials exhibit unusual properties is that, as the physical scale becomes very small, a larger proportion of atoms are found at surfaces or interfaces. For example, in a 3-D nanostructured material with a grain size of 10 nm, the proportion of atoms at grain boundaries approaches 50% (depending on the width of the grain boundary). This has a profound effect, not only on mechanical properties, but also diffusion, ionic conductivity and permeability.

Nanostructured coatings and structures can be fabricated by a number of processing methods. Nanoscale multilayers are generally formed by a sputtering or evaporative process performed in controlled atmosphere. Polycrystalline nanostructured materials are formed by consolidation of either very small particles or larger particles containing very small grains. The consolidation process involves the application of thermal energy and the challenge is to carry out the consolidation without engendering excessive grain growth. Last year, the Office of Naval Research launched a new program with the goal of producing nanostructured coatings for a variety of applications using thermal spray processing. These include resistance to wear, erosion, and cavitation. The feasibility of fabricating nanostructured thermal barrier coatings for gas turbine engines is also being considered. Thermal spray is attractive for several reasons. It is a very fast process, making it relatively easy to control grain growth. It is also an inexpensive process which is already in wide spread use. Implementation will not require any major capitol investment or extensive

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operator training. The program will concentrate on several materials including alloys, composites and ceramics. Development of TBC's will mostly deal with composites containing zirconia.

The changes in mechanical properties and thermal conductivity which can be obtained in an ultrafine materials can, potentially, be exploited to produce thermal barrier coatings which are, in some way, superior to a coating of the same material, but with conventional microstructure. Whether or not such coatings are possible depends on resolving several issues:

1) What grain size must be achieved to obtain significant improvement in thermal resistivity and mechanical properties such as toughness and resistance to cracking and spallation.

2) Can a suitable nanostructured material be synthesized at reasonable cost and in adequate quantity?

3) Can the synthesized material be processed into a coating which retains the nanostructure?

4) Can a nanostructured coating be fabricated with sufficient thermal stability to withstand typical service temperatures experienced in a gas turbine engine?

As will be discussed below, research to date indicates that it *may* be possible to produce nanostructured thermal barrier coatings for gas turbine engines which exhibit significantly enhanced properties and which are relatively inexpensive.

Properties of Nanostructured Ceramics

The properties of a nanostructured material can differ radically from a coarser material of the same composition. Understanding of these properties is very incomplete, especially those of nanostructured ceramics. This is partly due to the fact that until recently, it has been very difficult to fabricate good quality test specimens reproducibly. Some properties important to consideration of TBC's have been well documented. For example, it has been widely observed that nanoscale ceramic particles have greatly suppressed melting temperatures and also sinter remarkably well at relatively low temperature (Ref 1). This is due to the very large surface area leading to a very large surface tension (producing a high effective pressure) and extreme reactivity. The high surface energy also leads to the stabilization of phases favored by the higher pressure. For example, the ambient stable phase of zirconia particles smaller than a critical size is rutile. Coarsening produces a transformation to anatase. The critical size is temperature and purity dependent, about 30 nm at room temperature. This is illustrated in Figure 1. A consequence of this stabilization is that the use of yttria must be reexamined. Normal compositions of YSZ are greatly over

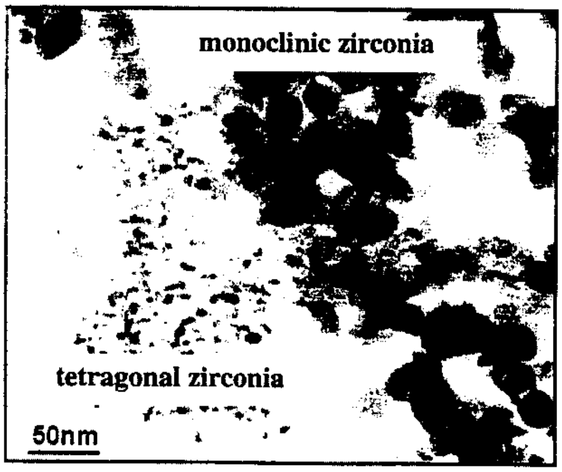

Figure 1. Zirconia noparticles above (anatase) and below (rutile) critical size. (Courtesy of C. Berndt)

stabilized and exhibit no transformation toughening. The toughening mechanism reappears if the percentage of yttria is reduced to below 2 percent (Ref 2). Another important feature of nanostructured ceramics is reduced thermal conductivity (Ref 3). This effect results from the grain boundaries being closer together than the typical distance between point defects in a conventional ceramic. Thus, the grain boundary contribution to phonon scattering becomes anomalously high. The calculated phonon contribution to thermal conductivity is illustrated for zirconia (figure 2) and YAG (figure 3). In both cases, the thermal conductivity at room temperature is dramatically reduced as the grain size goes below 100 nm, the traditional definition of a nanostructured material. However, the drop in thermal conductivity at operating temperatures within gas turbine engines becomes significant only when the grain size goes below about 20 nm. Several unpublished studies have demonstrated that this is indeed the case. Not shown in the calculations is the photon contribution to thermal conductivity. This is of major importance since nanostructured zirconia is quite transparent to infrared. Therefore, a nanostructured TBC' would have to include micron size inclusions, either pores or a suitable second phase.

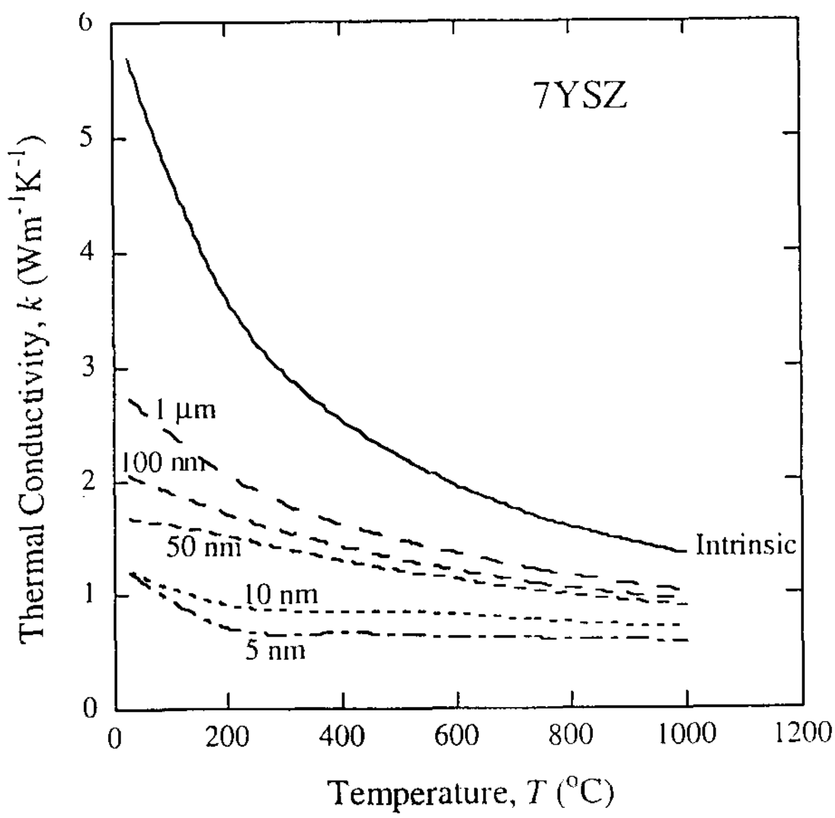

Figure 2. Thermal conductivity of 7YSZ versus grain size and temperaure (Ref. 3)

It was previously observed that it is difficult to consolidate nanostructured powder without excessive grain growth. This is illustrated in figure 4, which shows final grain size as a function of sintering temperature (Ref 4). Two things are evident. Grain growth becomes significant as temperatures approach 800 C. Also, porosity is not effective in inhibiting grain growth, as can be seen by the fact that sintering of green bodies with differing porosity result in the same final grain size. This implies that grain growth in service would be a problem. Clearly, a monolithic nanoceramic cannot be used as a TBC in a gas turbine engin. The material must be a composite, moreover one containing immiscible phases. Some research has been done on a composite of zirconia and alumina. Coatings were fabricated by atmospheric plasma spray using several different sources of nanostructured starting materials. It was found that the percentage of alumina needed to stabilize the structure depended considerably on the morphology of the thermal spray feedstock and, therefore, the morphology of the coating. In the best coatings, 30 % alumina stabilized the grain size and, therefore, tetragonal phase up to 1100 C (Ref 5). A very fine grain size (below 20 nm) could not be achieved because there was complete melting

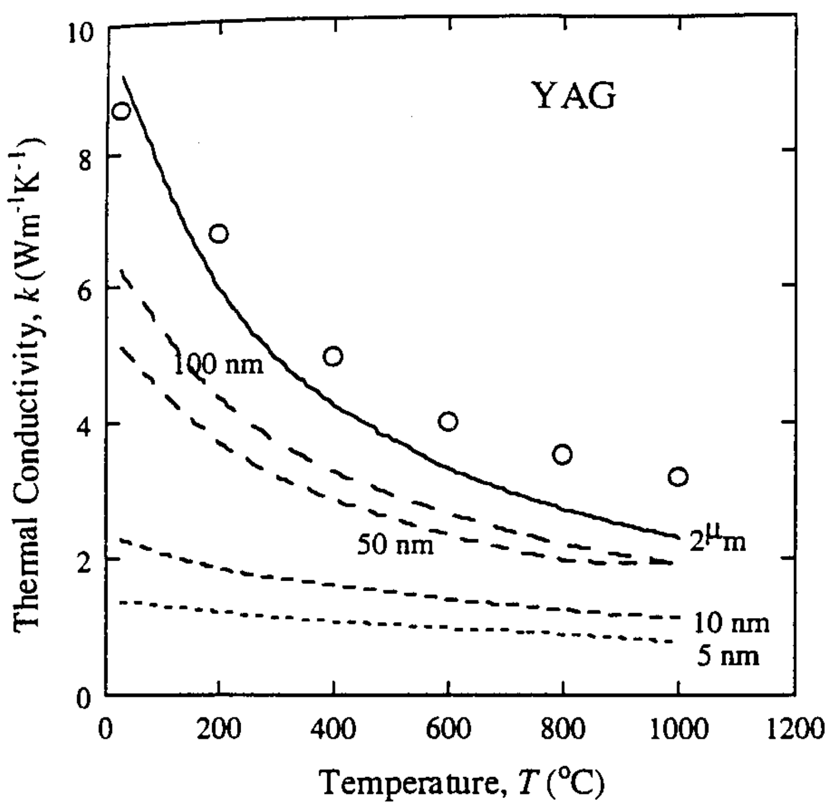

Figure 3. Thermal conductivity of YAG versus grain size and temperaure (Ref. 3)

of the sprayed powder during processing. The grain size was limited by the quench rate and the phase separation of zirconia and alumina during solidification. The critical size for stabilization of rutile was larger in the composite than that found in individual pure particles. Typical grain size in these studies was 30 to 50 nm.

The mechanical properties of nanostructured ceramics depend critically on composition and microstructure. Almost all of the studies have been performed on "fully dense" material (in reality, unintentionally porous). Very little work has been done on intentionally porous materials, as one would prefer to have in a TBC. In spite of the lack of a large body of definitive data, two facts emerge. Nanostructured ceramics deform superplastically at moderate temperature (Ref 6). This temperature is typically less than half the melting temperature and can be even lower for very small grain size. It has also been observed that intrinsic stress can be relieved at low temperature, perhaps even room temperature. Room temperature relaxation has definitely been observed in nanostructured cermets (Ref 7). It was also observed in nanostructured titania by Gleiter (Ref 8). Gleiter attributed this to very high room temperature diffusion (more than six orders of magnitude higher than that found in microscale

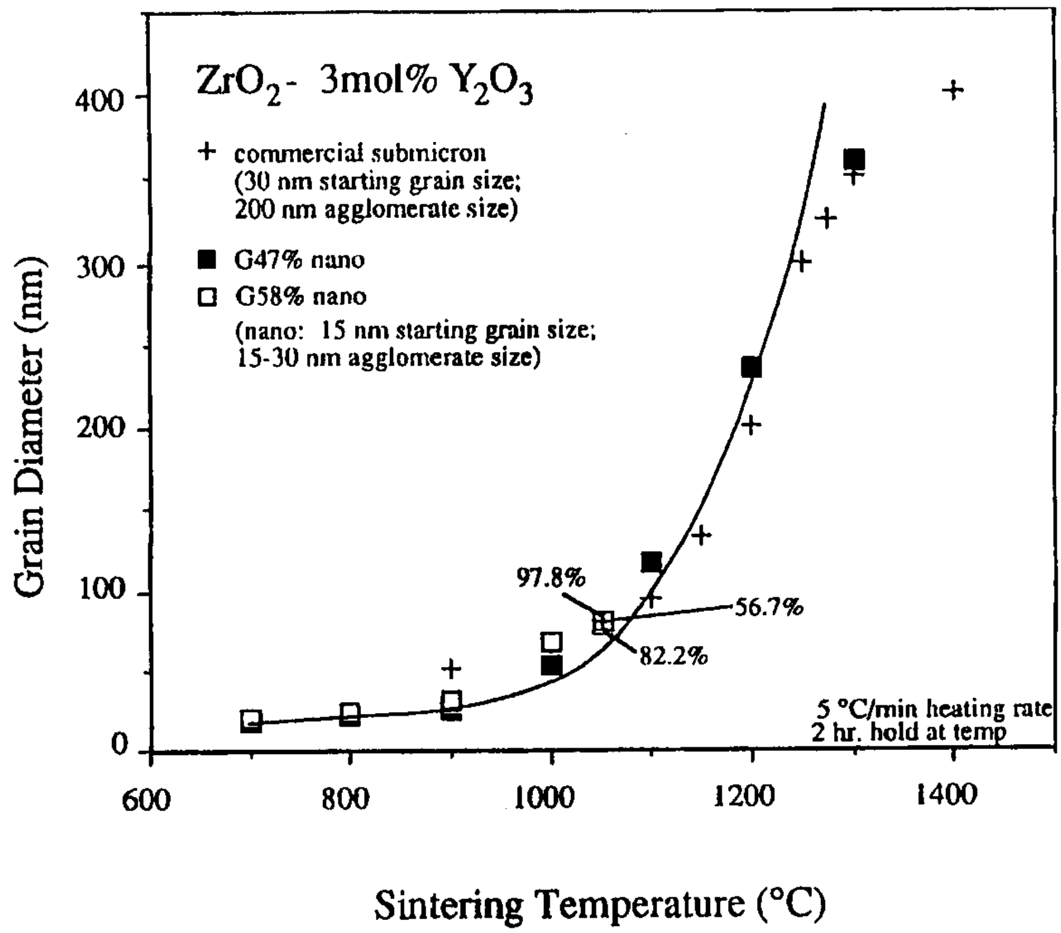

Figure 4. Grain size versus temperature for sintered nanoscale 3YSZ powder.

materials). It is clear that these coatings should not be used in situations where creep resistance is required. Another property affected by the ultrafine microstructure is fracture toughness. In the case of thermally sprayed nanostrucured zirconia, the biggest effect may depend on the way the coating is formed. If the feedstock consists of agglomerated small particles, such as colloidal material, and no melting (or only partial melting) occurs, then the coating will lack the splat boundaries present in conventional coatings. These splat boundaries are a major factor in the failure of conventional thermal sprayed coatings. It is possible to form coatings without melting because of the very high sinterability of the small particles. Moreover, use of such small particles is necessary if one wants to achieve a grain size small enough to effect thermal conductivity. If melting does occur, the coating will still be nanostructured provided the sprayed material is a composite of immiscible phases. In this case, the thermal conductivity will not be greatly reduced, but the mechanical properties will still be enhanced. Several companies are pursuing both strategies, but the information is considered proprietary at this time.

Discussion and Conclusions

The first requirement for successful fabrication of nanostructured TBC's be to obtain suitable material for thermal spray. The synthesis of suitable sprayable material has not been difficult. Nanoscale ceramic powder can be synthesized by gas condensation, by sol gel and colloidal processes, by various flame and plasma processes, and mechanical attrition. Several techniques have also been developed for reprocessing raw powder into a suitable form for thermal spray. These reprocessing techniques are proprietary and cannot be disclosed at this time. At present, commercial manufacturing of large quantities of nanoscale ceramic powder does not exist. Several companies have the capability to provide production capacity, but will need to see an adequate market before doing so. Research quantities are easily obtained from numerous sources.

Development of techniques for fabricating coatings by thermal spray are at a very early stage. It was noted above that improvement of thermal resistivity will require an extremely small grain size, of the order of 10 - 20 nm, while improvement of mechanical properties can be achieved by reducing grain size only to about 30 - 70 nm. The difficulty in retaining an ultrafine microstructure in the coating during processing an subsequent exposure to elevated temperature increases dramatically with reduced grain size. One reason for this is that the driving force for grain coarsening is highly grain size dependent. Another reason is that, while it is possible to produce a 30 - 70 nm grain structure through melting and rapid solidification, a 10 - 20 nm grain structure can only be achieved by avoiding melting, relying instead on rapid sintering of very fine particles. This may, if fact, be quite feasible, but it has yet to be demonstrated. Clearly, improving mechanical properties will be much easier than reducing thermal conductivity. In both cases, control of coating microstructure will require very tight control of the thermal history of the sprayed particles. This, it turn, will require excellent control of both the size and morphology of sprayed particles, and spray conditions. It may, in fact, require real time process control at a scale not currently available. Thus, it may be necessary to extend the state of the art in thermal spray. This much more likely to be true for improvement in thermal conductivity than for improvement of mechanical properties. Finally, a great deal of research still needs to be done in order to determine exactly what composition and microstructure to attempt to achieve. This will include a thorough study of creep and stress relief in the coatings.

In conclusion, the use of nanostructured TBC's with enhanced properties relative to existing materials is possible. It will require a great deal of effort both in research on nanostructured ceramic composites and in development of thermal spray techniques capable of achieving desired microstructures. The kind of effort required to reduce thermal conductivity will be quite different from that required to improve mechanical properties, with very different attendant risks. Ongoing work under the ONR program should clarify most of these issues during the next year.

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