4. ENABLING TECHNOLOGIES

A. Joining of Advanced Materials by Plastic Deformation

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Objective

- Join advanced materials such as ceramics, cermets, intermetallics, composites, biomaterials, etc., by plastic deformation, collaborate with industry and universities to produce sensors.
- Characterize the interfaces using scanning electron microscopy and fracture tests.
- Investigate grain rotation that is assumed to occur during grain–boundary sliding resulting in deformation bonding.

Approach

- Apply a modest compressive load to two pieces of similar or dissimilar materials that have had little surface preparation in the temperature region where the materials are known to deform by grain-boundary sliding.
- Examine interfaces by scanning electron microscopy.
- Measure residual stresses after joining dissimilar materials and compare to finite-element analysis.
- Measure strength of the interface by 4-point bend tests.
- Characterize electrical properties of sensors.
- Use electron back-scattered diffraction to measure grain rotation as a function of strain.
- Prepare for in-situ Advanced Photon Source experiment to measure grain rotation during deformation.

Accomplishments

- Strong, pore-free joints have been made with various ceramics, cermets, intermetallics, composites, and more recently, biomaterials, with and without various interlayers, fracture occurs away from interface.
- Patent application applied for oxygen sensor with internal reference.
- R&D 100 Award for oxygen sensor.

Future Direction

- Joining intermetallics to ceramics, joining biomaterials.
- Use functionally graded materials to distribute and reduce interfacial stress concentrations.

- Measure in-situ grain rotation during deformation or joining using the Advanced Photon Source, pending completion of installation of Materials Testing System in beamline and available funding.

Introduction

Joining by plastic deformation has been successfully applied in this program to various advanced ceramics (yttria-stabilized zirconia (YSZ)/alumina composites, mullite, SiC and TiC whiskers in a zirconia-toughened alumina (ZTA) matrix, metal-matrix composites and even an electronic ceramic, $La_{0.85}Sr_{0.15}MnO_3$ [1-5] or a bioceramic, hydroyapatite [6]. Techniques have been developed to minimize sample preparation procedures and the temperature at which the joining takes place, amongst them a spray applications technique [2] or use of nanocrystalline powders or dense interlayers stand out [2, 3]. We have formed pore-free joints in Ni_3Al. We have been informed that a patent will shortly be issued; a new one has been applied for, and we are in the process of filing an application for another. We have been awarded an R&D 100 for one of the best technical inventions of 2005 for our work with Ohio State University in developing a very compact oxygen sensor with an internal reference. As the sensor requires no external gas reference and hence no external plumbing, it can be located directly in the combustion chamber allowing for rapid response.

Joining of optical materials is one area that we had not previously explored. Hence, this year we have investigated the deformation and joining of MgF2 as a model optical material. In this case, the quality of the bond can be determined by optical spectroscopy, namely Fourier Transform Infrared Spectroscopy (FTIR), because any porosity at the joint would scatter and cause an increase in the attenuation.

While there still remains considerable work in the area of joining by plasticity, including the joining of intermetallics to ceramics, a technologically important area, there remains one fundamental question. Namely, what is the mechanism of joining? Most, if not all, of the materials that we have been able to join deform by means of grain boundary sliding. As long as there is no cavitation, the strain, it is assumed, is accommodated by grain rotation in response to diffusion as a result of unequal atomic mobilities along grain boundaries. To our knowledge, grain rotation has never been measured in a ceramic. To answer this question, with the strong encouragement of Dr. Sidney Diamond, we have undertaken a program to determine if the assumption is valid, and if it is, how much do the grains rotate? Initial experiments were performed ex-situ using Kikuchi lines as observed in the electron back-scattered diffraction mode in a scanning electron microscope.

In what follows, progress in FY05 on joining of optical and biomaterials and production of the oxygen sensor with an internal sensor will be discussed in more detail.

Plastic Deformation of Hydroxyapatite and its Application to Joining

Hydroxyapatite (HA) is a very common biomaterial that is generally used as a coating over a non-biocompatible material for implants such as teeth. Of course, coatings can be inexpensively applied using a number of different techniques.

However, producing complex shapes by these techniques is difficult. Joining by plastic deformation presents a new possibility for production of complex pieces of HA. Therefore, the first phase of this work was to determine the conditions under which HA exhibits plasticity because the plasticity of HA has not been studied in detail.

HA was deformed in compression into steady state between 1175 and 1275°C in air. Details can be found in reference [6]. The principal results are shown in Figure 1 plotting the logarithm of the steady-state flow stress versus 10000/T for 4 strain rates. HA was capable of strains of ≈0.25 (25%) without cavitation or fracture. The stress exponent was very close to 1 indicating that HA deforms by a viscous flow mechanism. The activation energy of 354 kJ/mole is within a factor of 2 of what is observed for deformation of most oxides materials when normalized by the melting points. The above factors and the absence of grain shape changes as determined by transmission electron microscopy (see Figure 3) are consistent with a grain-boundary

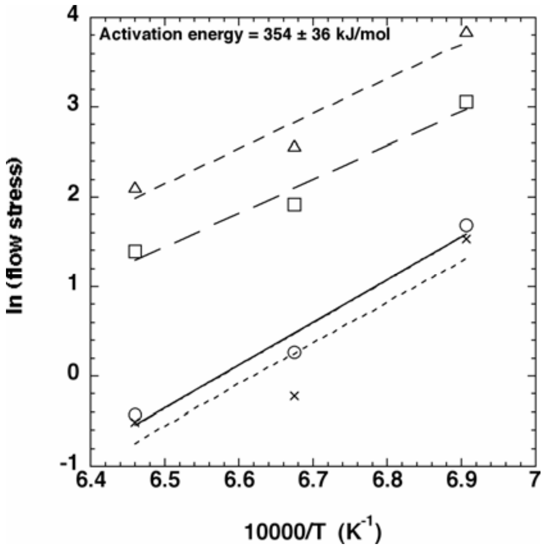

Figure 1. Flow stress as a function of test temperature at a constant strain rate (x: 5 x 10^{-6}/s; ○: $1x10^{-5}$/s; □: $5x10^{-5}$/s; Δ: $1x10^{-4}$/s.

sliding deformation mechanism. Note that the grains are clean and have not cavitated.

Using this information, two pieces of HA were successfully joined within the stress/temperature range in which HA exhibited extensive plasticity. A scanning electron micrograph of a joint formed at 1275°C at a strain rate of 1 x $10^{-5}s^{-1}$ is shown in Figure 2. Note that the joint, as indicated by the arrows, contains no porosity.

Optical Ceramics Case Study: MgF_2 Collaborators: J. Johnson, and J. S. Schlueter

MgF_2 was chosen as a case study representing optical ceramics because it is protypical of ceramics used in optical windows. MgF_2 transmits in the infrared (2-10 μm). Not only is the joining of optical materials important, but characterization of the joints by optical measurements affords another, and different, test of the quality of the bond. In particular, if the joint contains porosity the optical absorption will increase as a result of light scattering from the pores.

Two pieces of MgF_2 each having dimensions of 3x3x5mm were compressed together in our atmosphere-controlled Instron at 800°C in argon at a strain rate of $5x10^{-6}s^{-1}$. Surfaces were saw-cut from larger pieces with no further surface preparation. The MgF_2 had submicron grain sizes as shown in Figure 4.

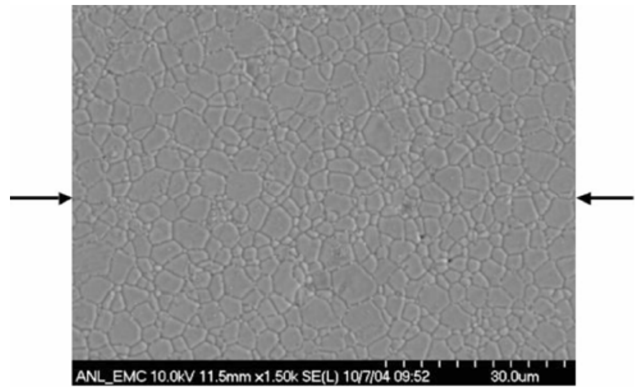

Figure 2. Scanning Electron Micrograph of HA samples joined at 1275°C at 10^{-5}/s strain rate; arrows indicate the joint interface.

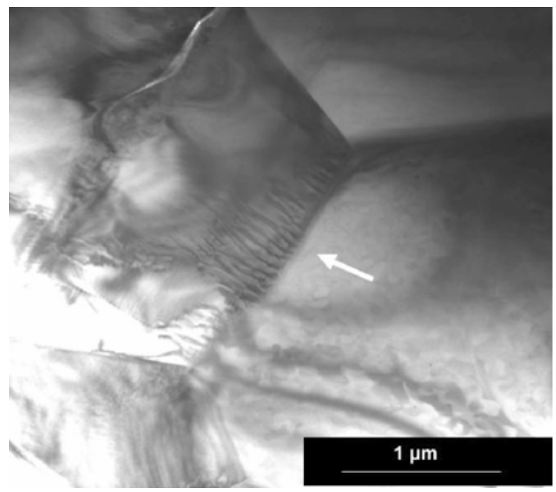

Figure 3. TEM micrographs of HA sample deformed at 1225°C.

SEM of the joined samples indicated that the porosity at the joint was equal to that in the bulk and hence the joint appears to be excellent. The more stringent test result is shown in Figure 5. In this figure the results are presented from the FTIR transmission measured from 3 areas of the unjoined and joined sample, compensated only at 2000 cm^{-1} using an absorption coefficient of 0.02 cm^{-1} for the different lengths of the optical path. The conclusion is that the joining does not affect the IR transmission.

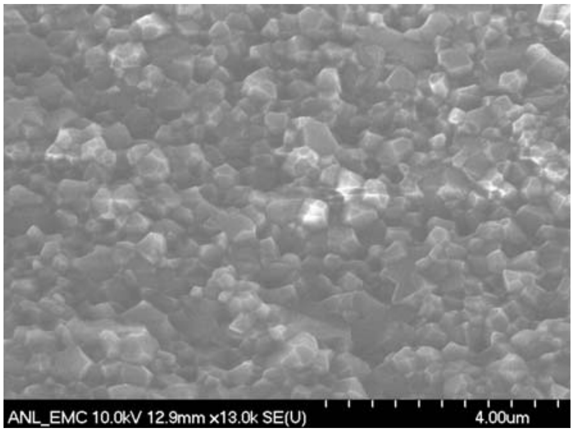

Figure 4. Scanning electron micrograph of the as-received MgF_2.

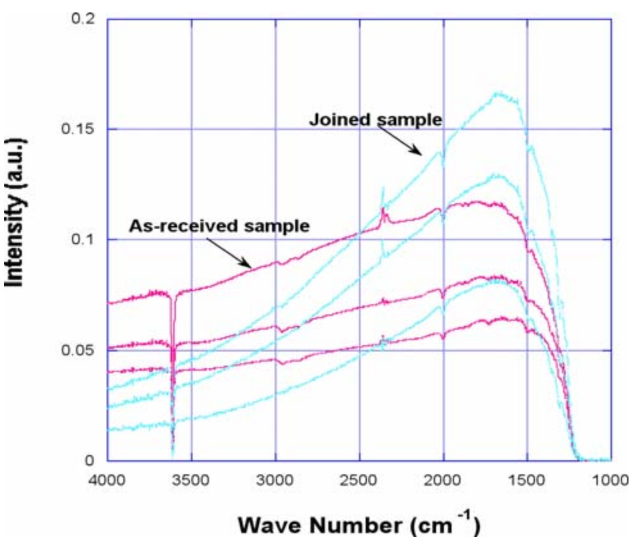

Figure 5. FTIR transmission compensated for optical path only at 2000 cm^{-1} obtained on unjoined and joined samples of MgF_2 (gray color, three locations on as-received sample, black, three locations on joined sample).

Air-Reference Free Potentiometric Planar Oxygen Sensor (Collaborators: R. Ramamoorthy, J. V. Spirig, S. A. Akbar, and P.K. Dutta, all of Ohio State University)

In the previous annual report the use of plastic deformation to form gas-tight seals that allowed the production of miniaturized oxygen sensors that contained metal/metal oxide powders was discussed. The use of an internal reference eliminates using an external reference gas and its costly plumbing equipment. Additionally, the sensor is more robust and can withstand the thermal cycling that causes cracks to form in the previous designs that required a ceramic-glass seal.

We have produced several sensors containing Pd/PdO powders. The output of these sensors is in agreement with the Nernst–Einstein relation. They have shown long-term stability, attesting to ability of the gas-tight seal to withstand thermal cycling. Several sensors have been sent to our industrial partners for long-term testing and possible licensing. The sensor is shown in Figure 6.

A patent application has been filed for the oxygen sensor. Another application extending the plastic deformation method of joining is in progress. OSU, Makel Engineering, and ANL have submitted a proposal to DOE's Office of Industrial Technologies, to use the plastic joining principal to produce a wide-variety of sensors. Most important, the oxygen sensor has won one of the 2005 R&D 100 awards.

Grain Rotation (collaborator, J. Johnson)

A critical experiment both from a basic and applied point-of-view is to determine if grains rotate while undergoing deformation by grain-boundary sliding. The literature is very limited for metals [7] and as far as we can determine, non-existent for ceramics. Recently simulations have shown that microstructual inhomogeneities can result in grain rotation during large-strain grain-boundary diffusion-assisted plastic

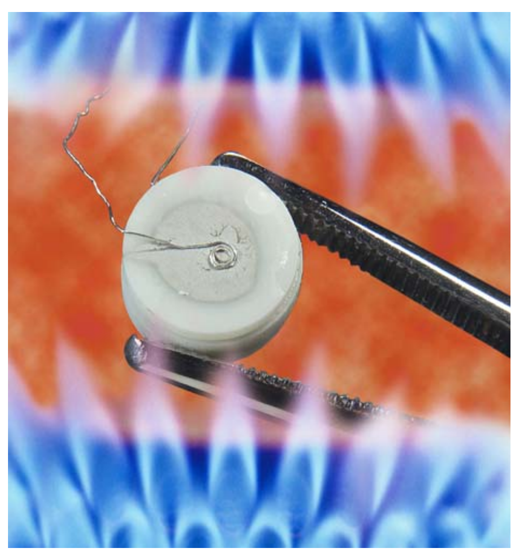

Figure 6. Oxygen sensor with an internal reference in simulated combustion atmosphere.

deformation [8]. Therefore, there is some theoretical justification to expect grains to rotate during deformation.

Our first attempt to measure the orientation of grains in a fine-grained polycrystalline ($BaTiO_3$) ceramic using the high-energy x-rays of the Advanced Photon Source was successful. The orientation of over 50 grains in the ≈6μm grain size sample was measured. However, rotation could not be measured because deformation was accomplished ex-situ and it was never established that the same grains were being illuminated after returning the deformed sample to the beam. This lead to the conclusion that experiments must be performed in-situ. Plans are underway to install a servo-hydraulic mechanical testing machine on one of the diffraction beam lines at APS. There are also plans to install an infrared heating source. Hence, it is anticipated that, depending on funding, in-situ grain rotation experiments will take place in the beginning of FY07.

However, in the meantime, we have measured grain rotation in 6 μm grain sized $SrTiO_3$ as a function of strain using electron backscattered diffraction. The $SrTiO_3$ sample was carefully polished and SEM was used to identify about 20 grains. Such an SEM image is shown in Figure 7. Microhardness indents were made to insure that we could locate and orient the same grains after deformation at 1300°C in steps of 0.02 strain. The movement points obtained from the Hough transformation of the Kikuchi lines (see insert in Figure 7) were used to determine grain rotation as a function of deformation.

The two grains shown in Figure 7 (#23 and #24) rotate as shown in Figure 8. There appears to be saturation after about 4% deformation. Interestingly, the amount of rotation observed is not that different from the amount predicted by the simulations of Coble creep that were performed for an ideal system [8]. We also measured the form factor for all 20 grains and it remains unchanged during deformation. Coble creep would predict that the grain shape must change in accord with the strain. That this is not observed is further evidence that creep in these fine-grained ceramics occurs via grain-boundary sliding.

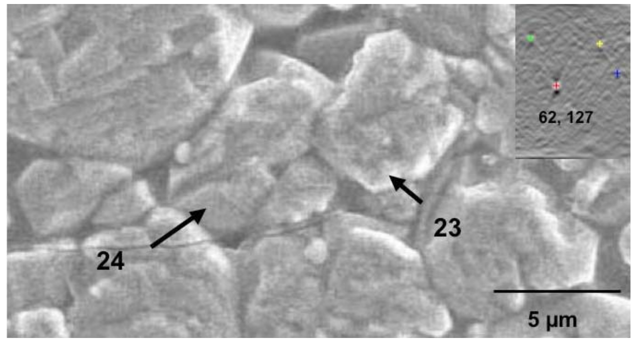

Figure 7A. SEM used to identify and orient two selected grains in undeformed $SrTiO_3$. Insert is the Hough transformation points of the Kikuchi lines from EBSD.

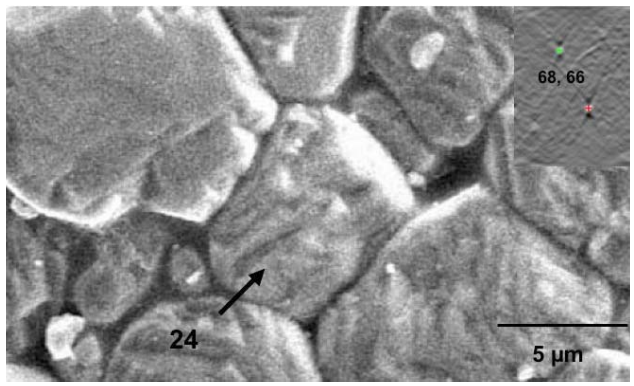

Figure 7B. SEM of same grains as shown in Figure 7A after strain of 0.08 at 1300°C. Insert is the Hough transformation points of the Kikuchi lines from EBSD.

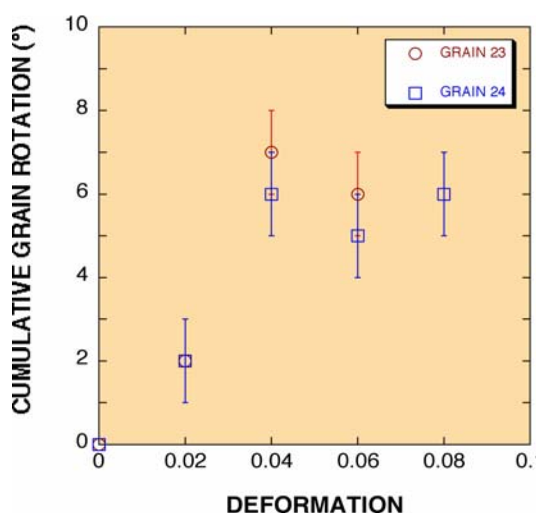

Figure 8. Cumulative rotation of grains 23 and 24 as a function of strain.

The nature of the rotation is a very statistical process as illustrated in Figure 9 in reasonable agreement with the simulation studies [8]. This figure shows the cumulative rotation for seven of the grains. Much theoretical and experimental work remains.

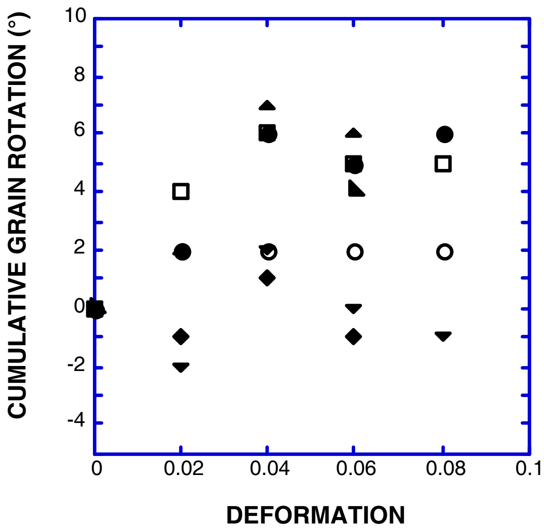

Figure 9. Cumulative grain rotation angle as a function of strain measured for seven grains, each shown by a separate symbol. This illustrates the statistical nature of the rotation.

Conclusions

We have shown that we can form pore-free, very strong joints in a wide-variety of important materials by plasticity. We have reported on joining structural and electronic ceramics, metal-matrix composites, Ni_3Al, whisker-reinforced ceramics, and cermets, bioceramics, and optical ceramics. Little surface preparation and modest temperatures are required for deformation joining. Those factors make the process attractive for commercialization. Using the alumina/ zirconia system as a model material, we have shown that the fracture of a joined bar of the same composition has the same strength as the matrix. The fracture of a joined 4-pt bend bar of dissimilar compositions does not fracture at the interface, but at a position near the maximum residual tensile stress. The optical transmission of joined MgF_2 is the same as that of an as-received sample of MgF_2, providing yet another assessment of the excellent bond quality achieved by deformation joining.

We have applied the technique to a practical problem, namely, producing a gas-tight oxygen sensor. The sensor won an R&D 100 Award and a patent application has been filed. Furthermore, several sensors are out for industrial testing with the view of licensing. A new patent application is in preparation.

We have demonstrated, for the first time to our knowledge, that during grain-boundary sliding, grains rotate in a statistical nature to accommodate the strain. Grain orientations were determined by ex-situ electron back-scattered diffraction patterns. These experiments will set the stage for in-situ grain rotation experiments to be performed in the beginning of FY07, pending available funding.

In the meanwhile, we will perform joining experiments on intermetallics and metals to ceramics using the plastic deformation technique. We hope to be funded to continue and expand the work on miniaturized gas sensors.

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