LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-TR-223635

Mechanical Behavior of Grain Boundary Engineered Copper

S. B. Carter, A. M. Hodge

August 10, 2006

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Mechanical Behavior of Grain Boundary Engineered Copper

Sarah Carter, Dr. Andrea Hodge

7 August, 2006
Lawrence Livermore National Laboratory, University of California, L-353
7000 East Avenue, Livermore CA, 94550
s.carter07@cox.net
Dr. Brian Kennedy, Dr. Ashley Jones

Abstract

A grain boundary engineered copper sample previously characterized by Electron Backscatter Diffraction (EBSD) has been selected for nanoindentation tests. Given the fact that grain boundaries have thicknesses in the order of 1 micron or less, it is essential to use nanomechanics to test the properties of individual grain boundaries. The Hysitron nanoindenter was selected over the MTS nanoindenter due to its superior optical capabilities that aid the selection and identification of the areas to be tested. An area of 2mm by 2mm with an average grain size of 50 microns has been selected for the study. Given the EBSD mapping, grains and grain boundaries with similar orientations are tested and the hardness and modulus are compared. These results will give a relationship between the mechanical properties and the engineered grain boundaries. This will provide for the first time a correlation between grain boundary orientation and the mechanical behavior of the sample at the nanoscale.

Purpose

The purpose of our investigation is to determine the mechanical behavior of the individual orientations of grain boundaries within a grain boundary engineered copper sample and correlate the results according to the degree of order and orientation. By testing the hardness and modulus of individual grains and boundaries, we hope to expand on the existing data supporting a correlation. Using nanoindentation techniques, we hope to demonstrate that "special boundaries" or boundaries with a particular orientation and high degree of atomic matching are indeed stronger than other "random boundaries" and contribute to the overall increased strength of the material[1].

Hypothesis

Grain boundaries with a higher degree of order and orientation are projected to have stronger mechanical properties than random boundaries with little order. Using EBSD mapping, these boundaries can be identified and classified by the fraction of atoms that align in the region where the two lattices meet. Through direct measurement of the local hardness and modulus of the highly ordered grain boundaries and the random boundaries, as identified by the EBSD, the strength of these nanostructural features can be compared. These local measurements taken with nanoindentation equipment will be correlated with the EBSD mapping and are expected to show a trend that relates higher order to higher strength.

Introduction

Over the past several decades, scientists have utilized the technique of grain boundary engineering to enhance the physical properties of various metals and alloys. Grain boundaries are especially susceptible to corrosion due to the "atomic mismatch" where two grains or crystals meet[2]. Using thermomechanical techniques such as strain annealing, scientists have altered the overall grain boundary character distribution

(GBCD) and increased the number of “special boundaries” that have a stronger resistance to this corrosion. The intent of these techniques is to increase the metal’s microstructural resistance to fracture and intergranular decay[1].

Scientists have previously investigated the effects of grain boundary orientation on the mechanical properties of copper and similar materials based on the percent composition of the orientations; however, the properties of the individual grains and grain boundaries with these orientations have not been tested on a nanoscale. It has been determined that by processing copper and engineering the GBCD with respect to boundary orientation, susceptibility to creep, fatigue, embrittlement, and corrosion can be significantly reduced[3]. Intergranular cracks typically spread along the “random boundaries” within a sample, thus, by increasing the fraction of “special boundaries”, engineers are provide obstacles to the lengthening cracks and strengthen the sample[4].

Schwartz et al. recently modified the GBCD of a series of copper samples using varying methods of thermomechanical processing. They have provided one of their samples that resulted with a high fraction of special boundaries for this study. Electron Backscatter Diffraction (EBSD), a technique that uses a scanning electron microscope to map a surface, will be used to identify the special boundaries in our sample[5]. These boundaries are differentiated by the fraction of atoms in the region between the adjoining lattices that are aligned. For example, in a $\Sigma 9$ boundary, one ninth of the atoms along the boundary are aligned. Thus, the lower the sigma number, the higher the degree of order at the boundary. After undergoing the thermomechanical treatments, a high fraction of $\Sigma 3$ boundaries resulted, strengthening the copper sample[3]. Using the EBSD mapping, we will identify the “special boundaries” and compare the hardness and modulus of these boundaries with those of the "random boundaries" and typical grains. From this comparison, we should be able to extend our analysis of the properties of copper to the intergranular interactions.

This investigation of properties on a nanoscale is important to the scientific community as we pursue nanoscale synthesis in our laboratory. The Lawrence Livermore Lab houses the Nuclear Ignition Facility (NIF) laser and is continuing the study and production of nanotargets for use in 2010. As we expand our knowledge of nanoparticles and nanoscale properties, we are preparing for the upcoming experiments with the NIF laser.

Procedure

- Begin with a pure copper sample that is large enough to undergo multiple rolling deformation treatments and still be intact. Measure the thickness of the sample and calculate a 20% reduction in thickness. With many passes, roll the sample using an adjustable rolling device until it has undergone a 20% reduction in thickness. The device can be adjusted using a series of cranks and gears to reach the desired width. Test shims with predetermined thicknesses are used to ensure that the width of the gap in the rolling device is the desired thickness.
- Heat-treat the sample at 560ºC to relieve the stress on the sample during the deformation treatments.
- Repeat the deformation and heat treatments, each time obtaining a 20% reduction in thickness, until an overall reduction of 67% is reached. This series of sequential rolling and annealing treatments has been proven to be the most effective in

modifying the GBCD of the copper sample. It increases the number of Σ3 boundaries within the sample, giving it more order and strengthening the sample.

- Polish the sample using the polishing wheel and the accompanying grit papers. As the grits progress higher, 600 to 800 to 1200, the roughness decreases and the grits create fewer scratches on the sample. Each time you progress to a higher grit, rotate the orientation of the sample with respect to the direction of the wheel by 90º. This will make it easier to check that the sample is being polished correctly and that the large scratches from the previous grit are being eliminated. After using each grit, view the sample in the optical microscope to ensure that no large scratches are still visible before moving on to a finer grit.
- After progressing through all of the grit papers, move on to diamond slurries. These are finely gritted solutions that are used with cloth discs on the polishing wheel and the sample is not held in one orientation throughout the process. The sample is moved around the wheel in the opposite direction of the spin in order to get a uniform distribution of small scratches. Decrease the grit from a 9 micron diamond slurry to 1 micron to .25 micron, checking under the optical microscope each time.
- Blow dry (do not towel dry after polishing) and store the samples in a desicator cabinet to minimize grain growth and oxidation.
- In order to identify the equipment that will give the best results, run a simple nanoindentation test on a sample piece of copper using both the MTS and Hysitron nanoindenters. The MTS nanoindenter is an older machine that is not as precise as the Hysitron, however, it is much easier to operate. The downfalls of

the MTS also include the size requirements of the samples, the less advanced analysis software, and the fact that it has been experiencing software difficulties over the past few months.

- After concluding that both the MTS and the Hysitron would perform adequate tests on our samples with average grain size of 50 microns, it was determined that it was necessary to use the Hysitron due to its superior optical capabilities. The imaging software and optical microscope of the Hysitron assist us in matching the test area to our EBSD map. Testing the correct boundaries and areas with precision is the most important aspect of the nanoindentation process.
- Using the Vickers indenter, mark three 2mm by 2mm square regions on the sample surface. The Vickers indenter is best qualified for this procedure as it uses much larger loads yet still has optical capabilities for measurement. Mark the corners of the three regions with 100g load indents, differentiating one corner from the rest using 50g load indents nearby. This will aid in identifying the areas to be mapped using the EBSD and again finding those areas with the nanoindenter imaging software.
- Create a map of the sample using Electron Backscatter Diffraction. This system is paired with the scanning electron microscope, and will provide a clear, color-coded map of a small region of grains and grain boundaries on the sample surface. Determine which boundaries and grains have highly ordered orientations, such as $\Sigma3$ and $\Sigma27$, and which are random boundaries that have no specific connectivity. The random boundaries will serve as the control group to aid in comparing the hardness and elasticity of the special boundaries. We had initially marked three

squares for mapping so that we could select the best of these EBSD maps to use in our study.

- After obtaining the EBSD map of the sample, mount the sample using white out on a magnetic disc. White out is easy to remove, yet firm enough to not alter the data we gather from the nanoindenter. Place the sample on the magnetic nanoindenter stage and locate it with the built in optical microscope.
- Calibrate the optics and stage offset using the Aluminum sample designated for calibration. When calibrating the machine, run a pattern of indents with a large load such as 9000 microNewtons (μN) and then optically locate the center of the indent pattern.
- After the machine has been calibrated, define the outer boundary of the sample and run a quick approach to the surface at its center.
- Optically locate the region of the EBSD mapping and select a large grain nearby in order to determine an appropriate load function and indent spacing.
- In this study, 1000 μN was selected as an appropriate peak load. This peak load, the loading rate, and the tip shape (a Berkovich tip with a pyramidal shape) will be kept constant for every indent throughout the study. A Hysitron tip has a diameter of 200 nanometers and can be precisely directed into the sample surface with a specific load function. The program collects data regarding the displacement of the tip into the sample and the force applied by the tip. From this data, the program displays simple graphs of the Force vs. Displacement, and can then determine the hardness and elastic modulus of the sample for each indent. The program also tracks drift, error, and calculates the standard deviation when

multiple plots are combined. In combining multiple plots, the program allows the direct comparison of multiple indents and types of indents.

- In testing the grains, a simple method approach can be used to run a series of indents in a grid pattern. This technique requires an identified position (located optically), a load function, an indent pattern, and a designated location to save the data. This is a quick and simple way to gain data points if they do not need to be preciseky aimed at a grain boundary.
- When indenting on the grain boundaries, utilize the scanning mode of the indenter software that will allow you to see differences in texture. This imaging scan uses the indenter tip to gather topographical information about a small region (as small as 10 microns square) to aid in identifying a precise location of a grain boundary.
- The data that is most helpful for this analysis is the Force (μN) vs. Displacement (nm) graphs, the hardness, and the elastic modulus. The results of the tests should show a correlation between the hardness (GPa) and modulus (GPa) of the grain boundaries and their orientations.

Upcoming goals and deadlines for project:

- August 7th – Presentation and paper drafts complete.
- The study will continue will data collection and the organization of results until August 18th. By the 18th, I plan to have data for at least one type of organized boundary and data from random boundaries for comparison. Data collection will continue at the laboratory after I leave on the 18th, but I plan to have at least one category of boundaries well underway before I leave. I will continue to collect

data until the 18th and get it released so that I may continue to analyze the results after I have left the laboratory.

- September 1st – Drafts resubmitted with data/results, analysis, and conclusion complete.

Materials

- Pure copper
- Rolling device with adjustable widths
- Programmable heating furnace
- Polishing wheel, polishing grit paper and solutions
- Mounting supplies
- Vickers Indenter
- Electron Backscatter Diffraction Microscope
- Scanning Electron Microscope
- MTS nanoindenter
- Hysitron TriboIndenter®
- Optical Microscope

Results

The results of our nanoindentation tests are automatically saved to the computer, but we also keep each grid test (this can range from 4 to 100 indents) and each individual indent labeled and categorized on the computer and filed away for later recall. After each run of the indenter, the data is organized into a Force vs. Displacement graph (sample shown in Figure 1) and graphs of the Hardness and Reduced Modulus (sample shown in Figure 2). These graphs are printed and labeled and placed in our project journal with accompanying notes on data points that should be removed and derivations from the expected result.

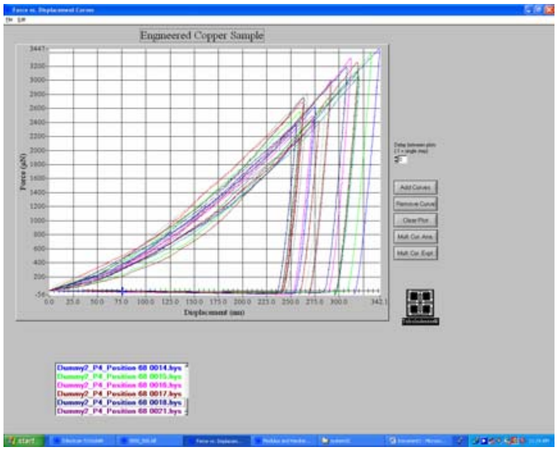


Figure 1.

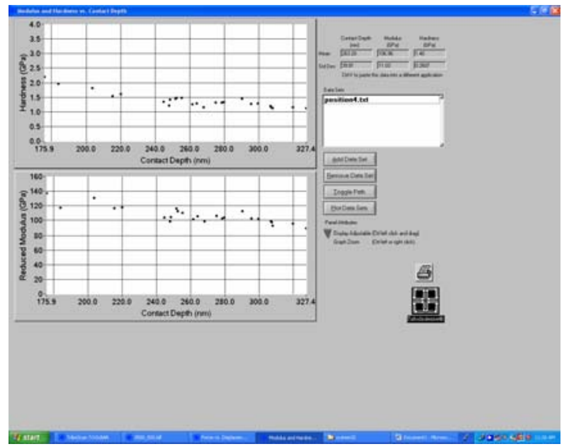


Figure 2.

We can also save scanned images from the indenter software to keep track of indents made on individual boundaries as seen in Figure 3. All of this data is dated and named appropriately when inserted in the journal.

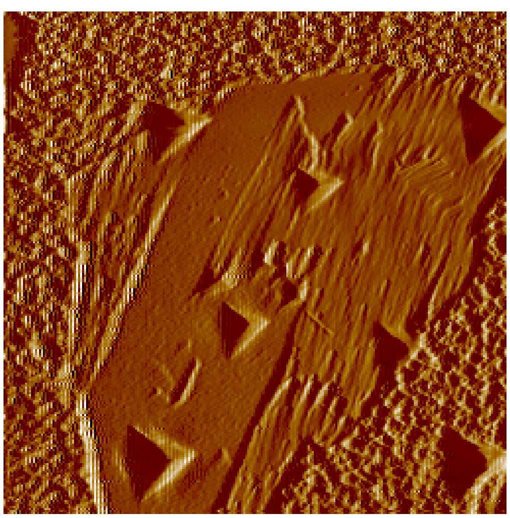


Figure 3.

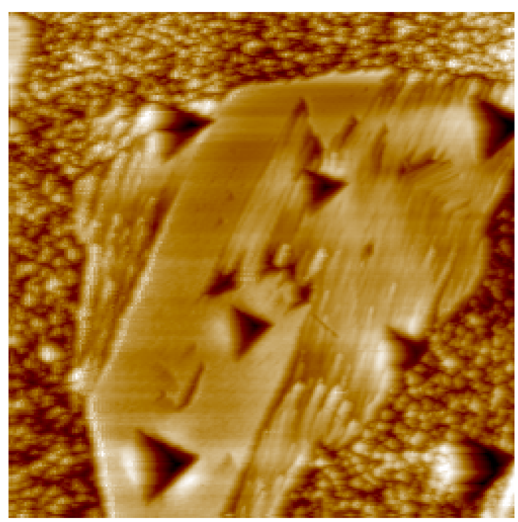
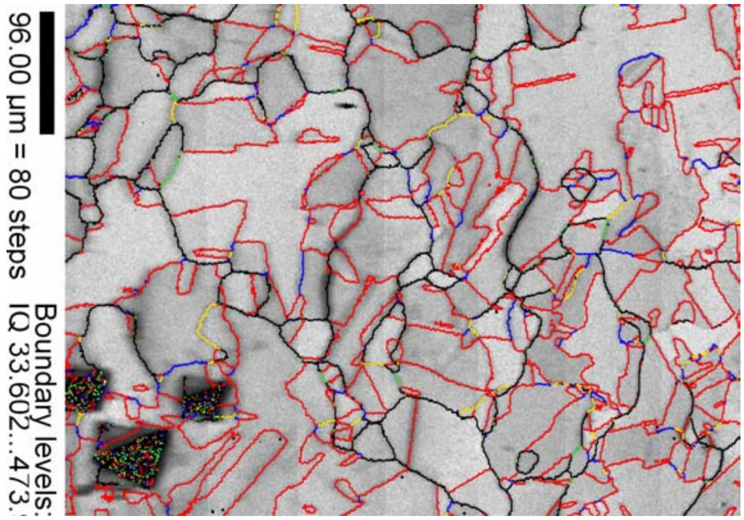


Figure 4.

Analysis

In analyzing our data, we will categorize it by the spatial location on the EBSD map. There should be little difference in the data from similar parts of the grain boundary network, however we hope to see a variation in the results from differently oriented boundaries.

EBSD mapping –
Cu 560 - S



Individual data points that fit into a single orientation group could be organized into a chart for averaging and finding irregularities.

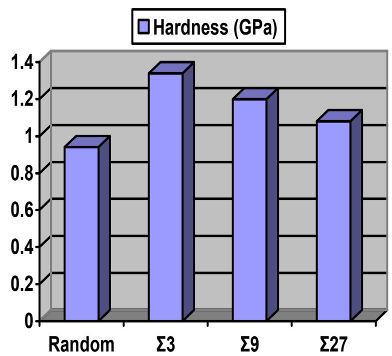
Specification / Orientation 1 :			Specification / Orientation 2 :		
Sample	Hardness (GPa)	Modulus (GPa)	Sample	Hardness (GPa)	Modulus (GPa)
1			1		
2			2		
3			3		
…			…		
Average			Average		

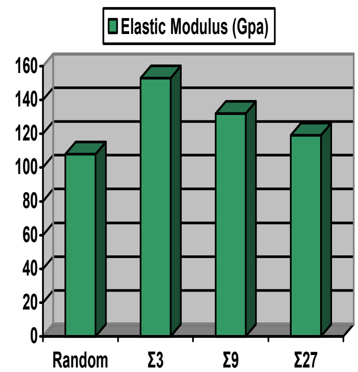
Then these averages could be organized into a chart for comparison.

Grain Size and Specification	Grain Orientation / Angle	Hardness	Modulus

The hardness and modulus data could also be organized into a bar graph to emphasize the scale of the differences in properties.

Sample data shown below. Actual results still to come as tests are still underway.





These results will prove that the composition of the material with respect to "special boundaries" has a direct affect not only on the macroscopic properties, but also on the strength of the material on a small scale. Or, the data could show us that the small-scale properties are independent of these "special boundaries". If there is no direct correlation between orientation and hardness, or the data is inconclusive, our hypothesis will not be confirmed, however, it is anticipated that we will learn that the correlation does carry over to the nanostructural level.

Conclusion

- Is there a correlation between orientation and strength within grain boundaries?
- How accurate were our measurements and mapping when we gathered our results?
- Is this correlation strong enough to promote further investigation into nanoscale properties resulting from grain boundary engineering?

With the help of the EBSD mapping, we should be able to find a strong connection between the orientation of the grain boundaries and the strength of the material as shown through the hardness and modulus. Having been previously engineered to improve their grain boundary character distribution through strain and annealing treatments, these samples have already been analyzed and have proven to exhibit enhanced macroscopic mechanical properties. We hope to show that this is not simply a macroscopic result based on the fraction of “special boundaries” but also a microscopic result originating from the individual boundaries themselves.

Hopefully, our project will open the doors to more investigation of properties on a nanoscale. In the nanosynthesis lab, we hope to discover variations in materials and their properties that will allow us to enhance our knowledge of nano-scale mechanics.

References

(1) Gao, Yong, et al. "High-Cycle Fatigue of Nickel-Based Superalloy ME3 at Ambient and Elevated Temperatures: Role of Grain-Boundary Engineering." Metallurgical and Material Transactions A 36A (Dec. 2005): 3325-3333.

(2) Callister, William D. Materials Science and Engineering: An Introduction. New York: John Wiley & Sons, 1997.

(3) Schwartz, Adam J., Wayne E. King, and Mukul Kumar. "Influence of Processing Method on the Network of Grain Boundaries." Scripta Materialia 54.6 (Mar. 2006): 963-968.

(4) Schuh, Christopher A., Mukul Kumar, and Wayne E. King. "Analysis of Grain Boundary Networks and Their Evolution during Grain Boundary Engineering." Acta Materialia 51.3 (Feb. 2003): 687-700.

(5) Schwartz, Adam J., Mukul Kumar, and Brent L. Adams. Electron Backscatter Diffraction in Materials Science. New York: Kluwer Academic / Plenum, 2000.

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.