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14. ABSTRACT This PECASE award studied the similarities between amorphous and nanocrystalline alloys, in terms of their structure, thermodynamics, and mechanical properties. Three task lines in alloy design and processing, characterization, and mechanical property testing and optimization, were pursued in parallel, using both experimental and theoretical/computation methods. The work resulted in: (i) A new approach to control the grain size in nanocrystalline alloys, developed through the use of thermodynamic principles of metal glass formation; (ii)					
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Final Project Report for DAAD19-03-1-0235, “Mechanics of Metals with Grain Sizes Approaching the Amorphous Limit”, PI Christopher A. Schuh, MIT

Introduction and Problem Statement

This project sought to understand the structural and mechanical similarities and differences between amorphous and nanocrystalline metals. Both have exceptionally high strength, but are usually considered distinct materials classes and analyzed with rather different physical models.

We sought a unified description of both the structure and mechanics of these materials, with the ultimate aim of consciously designing the next generation of high-performance structural metals. Specific goals for the project included (i) development of new principles for the design of nanostructured alloys, (ii) identification of critical nanostructural scales at which alloys exhibit optimized properties under high-rate or impact loading conditions, and (iii) introduction of a practical route to optimized nanostructured alloys with scale-up potential.

The project involved three complementary task lines:

1. Alloy design and synthesis
2. Characterization of nanostructure
3. Mechanical property testing and optimization

In each of these task lines, both experimental and theoretical tools were brought to bear.

The present document is intended as a succinct but thorough summary of the achievements of the project, which ran for five years at MIT. All of the major goals of the program were met, including a successful technology transition and scale-up of a new nanocrystalline alloy in the commercial domain. This report covers the most important results attained over the project duration. As such, it summarizes many specific accomplishments also described in earlier interim reports; those reports may also be referred to for additional details. Many of the present results are also published in the open scientific literature. A complete list of publications resulting from this work is appended to the report.

Task Like 1: Alloy Design and Synthesis

This task line involved understanding the structural links between metallic glass and nanocrystalline metals containing alloying additions. Theoretical tools including atomistic simulations and analytical thermodynamics were applied to address this issue, leading to an improved understanding of how to stabilize a nanostructured metal. Experimentally, we developed a new processing science for controlling the grain size in

nanocrystalline metals over a very broad range, all the way to the amorphous limit. A summary of key achievements in this task line follows.

Theoretical Work:

1. We developed a significant modification of nonequilibrium thermodynamic alloy theory that helped to unify the understanding of nanostructured and amorphous alloys. Through atomistic simulations, we demonstrated that in addition to the usual thermodynamic temperature, kT , there is also a secondary, "effective temperature" that can be defined for nonequilibrium alloy systems, and which is governed by the size mismatch between atoms in the system and the means of processing the material. This new state-variable for nanostructured metals has helped us predict which systems will form nanocrystalline metals more easily, and the processing conditions required to do so.
2. We performed the first atomistic simulations to study grain boundary segregation in a nanocrystalline system. Using embedded-atom method potentials for the Ni-W system, we simulated nanocrystalline structures, and with conjugate gradient methods to maintain an equilibrium configuration, we added various concentrations of W to the structure. Employing Monte Carlo techniques, we evolved the structure to chemical equilibrium. We found that W has a tendency to segregate to the grain boundaries, and its composition in the grain boundaries is ~25%. This segregation significantly lowers the energy of the system, and stabilizes the nanocrystalline structure.
3. By building a free-energy based analytical thermodynamic model, we explored how segregating species influence the grain size of nanocrystalline alloys. Because the energy of the system may be lowered by segregation, higher solute content promotes finer grain sizes. When the global solute concentration reaches the equilibrium grain boundary concentration, a fully amorphous specimen is obtained. The system can be regarded as a "regular solution", but with additional intergranular contributions to the energy that lead to grain boundary segregation. Our model built on successful models in the literature, but is the most general model available and in particular can be applied to non-dilute systems such as we make experimentally; this is the first thermodynamic model of an alloy that smoothly connects the polycrystalline and amorphous states in this manner. With this model we rationalized our experimental data from electrodeposited specimens.
4. We also performed some atomistic simulations to explore the structural relationship between amorphous and nanocrystalline states, for alloys prepared through mechanical refinement techniques. Our approach allowed variation of the sizes of the atomic species in a binary alloy as well as the heat of mixing of the system, and helped us to clarify the structural relationships that occur when the length scales of the crystalline structure (i.e., grain size) and of the atoms themselves become similar. Although simplified, these simulations were the first of their kind and point to the critical lengths scales over which we should expect the most significant

structural variations, and called to the field's attention the critical role of alloying elements in mechanical refinement to the nanoscale.

Experimental Work:

1. An electrodeposition system was designed and assembled for the controlled synthesis of binary Ni alloys. The system incorporated closed-loop thermal control, tailorable in-situ agitation of the plating bath, and a robust current source that could be programmed to apply direct or alternating currents, as well as pulsed waveforms on a sub-millisecond time scale. The apparatus was extensively proof-tested on a variety of bath chemistries.
2. In the Ni-W system, we developed a new electrodeposition technique employing reverse-pulse currents. This technique led to nanostructured alloys in bulk form, with grain sizes as large as 200 nm (which is almost 10 times larger than previously achieved in this system), and as fine as ~2 nm (i.e., fully amorphous). We produced sheet specimens as well as small cylinders of uniform wall thickness. The use of millisecond-scale reverse current pulses, applied periodically during deposition, allows the selective removal of W from the Ni-W alloy, and can be used to control the final composition of the alloy. Because composition in turn governs the thermodynamically favorable grain size in the Ni-W system, this new development represented a novel method for controlling nanostructure; any grain size in the range 2 - 200 nm can now be consciously 'dialed in' in this system. A utility patent application was filed around this versatile new technology.
3. The new reverse-pulse technology described above allows unprecedented control over the structure of nanocrystalline metals, and this control can be exercised in-situ during the deposition process. We demonstrated the ability to create multilayered composite specimens with alternating grain sizes and graded grain sizes. The technique can be used to produce smoothly graded or step-graded structures. A prime application of these structures would be in damage and corrosion-resistant coatings.
4. Our invention on the control of grain size in Ni-W alloys led to a patent that was subsequently licensed by Xtallic Corporation (a start-up company founded by the PI), and commercialized. Xtallic Corp. scaled the plating technology to full industrial scale; as of this year (2009) more than 100,000 liters of plating chemistry have been used at locations around the world to render nanocrystalline Ni-W coatings with tailored grain sizes.

Task Line 2: Characterization of Nanostructure

This task line focused on detailed characterization of the Ni-W alloys produced in the work described above. Because these alloys have such fine grain sizes as well as complex alloy configurations, conventional electron microscopy methods were found to only provide baseline (qualitative) data about the structure. Accordingly, some more detailed work involving both structure simulation and atom probe tomography was carried out to better understand the alloy structure and its thermodynamic stability.

Theoretical Work:

1. Our nanostructured Ni-W alloys are stabilized by segregation of W to the grain boundaries, which lowers the grain boundary energy. In order to prove the presence of grain boundary segregation of W, we used atom probe tomography (which is described in more detail under the experimental tasks below). However, with grain sizes as fine as ~ 3 nm, there was no theoretical model capable of analyzing the atom probe data. Accordingly, we conducted complementary simulations using atomistic Monte Carlo methods to construct segregated nanocrystalline Ni-W, and then to query the kinds of chemical statistics that could be expected to arise in atom probe data. This model elucidated how composition distributions should appear in the atom probe, and validated the use of a W autocorrelation analysis to probe for grain boundary segregation. In the end, the modeling was critical to carrying out the experimental work.
2. We have also made significant theoretical progress in understanding the stability of nanocrystalline alloys through our analytical modeling effort. By considering the four processes of (i) grain boundary relaxation, (ii) grain growth, (iii) precipitation of intermetallics, and (iv) grain boundary segregation, we developed a microstructure evolution map for nanocrystalline materials with alloying additions. In addition to providing a view of the relative importance of these processes, the maps also graphically capture the level of stability that can be achieved by alloying in a nanocrystalline system.

Experimental Work:

1. We engaged in a formal collaboration with Dr. M. K. Miller at Oak Ridge National Laboratory, to apply 3-dimensional atom probe tomography to our nanocrystalline specimens of Ni-W. A graduate student, Mr. A. Detor, traveled to ORNL to prepare specimens and conduct the atom probe experiments. This work meshed with the simulation and analytical work described above, and provided a full 3-D map of the alloy constitution at the atomic level. The results verified that W has a slight segregation tendency, which promotes nanostructure formation. Our work was the first to examine nanocrystalline alloys across a range of grain sizes from 3 to 20 nm, and showed the mechanism by which alloying promotes finer grains.
2. One of the appealing features of these alloys is that the incorporation of W atoms promotes stability to thermally-activated structural changes. Accordingly, we conducted a major examination of the structural evolution of these alloys as a function of time-at-temperature during annealing. Although the heat treatment of nanocrystalline metals and alloys had been studied by many authors in the past, our study was the first one to systematically address all four major structural changes that can occur upon annealing a

nanocrystalline alloy. We explored grain boundary relaxation, grain growth, grain boundary segregation, and chemical short- and long-range order development in annealed Ni-W alloys. We combined many experimental methods, including calorimetry, x-ray diffraction, transmission electron microscopy, atom probe tomography, and microhardness testing, to provide as complete a picture as possible about structural changes that can occur in these alloys. We demonstrated that Ni-W alloys are remarkably stable with respect to unalloyed nanocrystalline metals, and offered some theoretical support to explain this result.

3. We extended our atom probe studies of nanocrystalline Ni-W to annealed samples. In so doing, we made a significant discovery about the nature of atom probe data in nanocrystalline alloys: after annealing, the grain boundaries in nanocrystalline Ni-W alloys are apparently restructured, rendering their imaging in the APT much simpler. For the first time in a nanocrystalline alloy, we were therefore able to use two complementary techniques to study segregation: (a) statistical analysis of the solute distribution without a priori knowledge of the grain boundary locations, and (b) examination of individual boundaries with known positions.

Task Line 3: Mechanical Property Testing and Optimization

An overarching goal of the project was to establish the mechanical/mechanistic similarity between the finest nanocrystalline alloys and amorphous metals. Our work in this vein included computer simulations as well as experiments. We studied the convergence of nanocrystalline with amorphous metals across the range of grain sizes that span the Hall-Petch breakdown (from about 20 to 2 nm).

Theoretical Work:

1. The conditions required to instigate plastic deformation in nanocrystalline and amorphous metals were studied in new detail using molecular simulation techniques. Building small representative volume elements of nanocrystalline and amorphous metals, we explored deformation under multiaxial loading conditions. We showed that neither of these materials obey the classical von Mises criterion, but must use a different criterion that is sensitive to internal friction. Furthermore, by identifying commonalities between the atomic motions in nanocrystalline and amorphous metals, we argued that the important mechanism controlling the strength and yield criteria of both materials is the same. Specifically, we believe that small 'shear transformation zones' of just a few atoms reshuffle under applied shear stresses, and these events are controlling for strength and related mechanical properties. In amorphous metals these zones can appear anywhere in the structure, while in nanocrystalline metals they are confined to intercrystalline regions. Additionally, our results agree very well with experiments, as described later.

2. We also conducted atomistic simulations to address the mechanics of dual-phase systems that incorporate both amorphous and nanocrystalline phases. In particular, we explored a simple binary amorphous system seeded with a single nanocrystalline inclusion. Our studies showed that there is a cross-over in length scales when shear bands in the metallic glass are of the same thickness as the particle diameter. For particles below this scale, the mechanical response is relatively unaffected; particles significantly larger than the scale of shear localization are required to see a change in the mechanical response.
3. We proposed a new meso-scale simulation method for deformation of amorphous and nanocrystalline metals. This technique involves combined finite-element and kinetic Monte Carlo simulation tools, and focuses on the dynamics of "shear transformation zones" as plasticity carriers in disordered metals. We developed and validated the code against statistical mechanics expectations for some simple situations. This model can be applied to understand the unique mechanical behavior of the finest nanocrystalline metals, with an emphasis on shear band formation.

Experimental Work:

1. We completed a detailed study of mechanical behavior of nanocrystalline Ni-W alloys with grain sizes ranging from 2 nm to 200 nm. This range of grain sizes spans the Hall-Petch breakdown regime, and our work in fact stands as the first truly systematic experimental study of the Hall-Petch breakdown. We revealed that below a grain size of about 10-15 nm, there is a transition from conventional dislocation-related plasticity to plasticity that is quite like an amorphous metal. This includes several interesting emergent behaviors at the finest grain sizes, including (i) a turn-over in the rate dependence of strength, (ii) a maximum in the pressure-sensitivity of strength, and (iii) the development of shear localization at the finest grain sizes. These observations provide some of the first compelling evidence that very fine nanocrystalline metals act like metallic glasses.
2. We extended instrumented nanoindentation testing methods in two critical directions: to high strain rates ($\sim 10^3$ /s) and to high temperatures (200 °C). This required modifications to our equipment and the development of new test protocols and procedures. These tests provided some critical new data as well. For example, we verified that as strain rate rises, there is an optimum grain size for the highest impact strength at about 12 nm. These results also helped to explain why the Hall-Petch breakdown sometimes appears as a plateau and sometimes as a peak; high rates promote the latter and quasi-static rates the former. Our high temperature indentation tests permitted the measurement of activation energies for deformation in nanocrystalline metals, giving insight on the mechanisms of deformation.

3. The applications of nanocrystalline metals and alloys of DoD relevance include a variety of armor and ballistic applications. Accordingly, the rate dependence of deformation and deformation mechanisms was a point of focus for the present project. In a collaboration with Dr. Eduardo Bringa and his coworkers at Lawrence Livermore National Laboratory (LLNL), we explored the shock loading behavior of our nanocrystalline metals. This interaction combined our expertise in preparing and characterizing nanocrystalline metals with LLNL's expertise in shock physics. Using laser shocks, we explored the deformed microstructures of nanocrystalline Ni.
4. Through the Singapore-MIT Alliance, in a collaboration with the National University of Singapore (NUS), a visiting NUS student performed Ph.D.-level work at MIT. Ms. Xiaoling Fu studied the relationship between amorphous and crystalline states in a complementary approach to our work on Ni-W. We completed the first systematic study of both low- and high-temperature mechanical properties in amorphous metals containing embedded crystalline phases, as a function the volume fraction of the crystalline phase. This work shed important light on the way in which the deformation mechanisms of amorphous and crystalline metals interact with one another, and in particular how the percolation of the crystalline phase is a critical factor determining whether an amorphous-matrix composite deforms more like a glass or a polycrystal.