INVESTIGATION OF MECHANICAL PROPERTIES AND THEIR RELATION TO THE
INTERNAL STRUCTURE OF NANOCRYSTALLINE METALS AND COMPOSITES

Technical Progress Report

For period 1 March 1993 - 1 July 1994

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ABSTRACT

TECHNICAL PROGRESS REPORT

1 MARCH 1993 TO 1 JULY 1994

Work on nanocrystalline metals has proceeded on three fronts: synthesis, characterization and property measurements. A new compaction unit has been installed that permits consolidation at elevated temperature. A recent SANS study of nanocrystalline Pd and Cu confirms the presence of pores of dimensions comparable to the grain size, as observed in the first SANS experiments. Extension of measurements out to high scattering angles indicated the presence of large amounts of hydrogen in the samples. Both qualitative and quantitative confirmation was obtained from prompt gamma activation analysis. It was found that compaction at elevated temperature, preheating the powders before compaction, or a post-consolidation anneal, greatly lowers the hydrogen content. The SANS measurements showed that annealing expands voids in samples with high hydrogen content, but voids shrink if the hydrogen has been removed. Measurements of elastic modulus in nanocrystalline iron has been carried out using a nanoindenter. The results indicate that the commonly observed diminution of modulus in nanocrystalline metals can be explained entirely on the basis of porosity. Detailed x-ray measurements have been carried out on nanocrystalline Pd to examine the frequency of twins and stacking faults. Results will be compared to TEM observations. Construction is underway of a new chamber for the inert gas condensation equipment, with the major goal of attaining a greatly improved vacuum.

TECHNICAL PROGRESS REPORT FOR THE PERIOD
1 MARCH 1993 TO 1 JULY 1994

The investigation of nanocrystalline (n-) metals and alloys is proceeding on three fronts. The first is the characterization of the internal structure of the samples as presently produced, particularly those aspects of the structure that impact mechanical properties. These characterization techniques will continue to be used as sample integrity improves. The second effort is devoted to the synthesis of new n-alloys, as well as to the improvement of sample purity and reduction of defects for all of our nanocrystalline material through advances in processing methods. The third thrust is the measurement of the mechanical properties of n-metals, with the goal of coming as close as possible to their intrinsic mechanical behavior.

Small Angle Neutron Scattering, Prompt Gamma Activation Analysis and Fast Neutron Activation Analysis Measurements of Cu and Pd

A second round of small angle neutron scattering (SANS) measurements was carried out at NIST October 1993 on several n-Cu and n-Pd samples. Some of the samples were made with the new compaction unit that permits compaction at elevated temperature. The temperature of compaction varied among the samples from 20 to 300° C. One was compacted at room temperature and subsequently annealed at 800° C. (See Table I.) Scattering measurements were carried out to a higher value of the scattering vector q than was done at the first SANS measurements. It became apparent that the scattering at the high q values, that had previously been ascribed to "nanovoids" one to two nm in diameter (following the observations of such small voids in n-Pd by positron lifetime measurements [1]), actually comes from hydrogen in the samples. This conclusion was confirmed by prompt gamma activation analysis (PGAA) measurements at NIST on several of the SANS samples. As

shown in Table I, the agreement between SANS and PGAA results is excellent. It is not known if the hydrogen is present as a gas by itself or combined with oxygen as water vapor. (The incoherent scattering cross section of oxygen is low and thus would not show up in the SANS measurements, whereas that of hydrogen is very high.) In any case, the amount of hydrogen in samples of both Cu and Pd compacted at room temperature is a surprising 5-7 atomic per cent. (Comparable amounts were found in n-Fe.) The hydrogen content drops with rising temperature of compaction, with heating of powders in the compaction unit preceding consolidation, or with post-compaction anneal.

The scattering from most of the nanocrystalline samples was found to be dominated by Porod scattering, with the incoherent scattering I_{inc} from the hydrogen also making a contribution. The behavior predicted by Porod [2] for the q -range such that $qR \gg 3$, is:

$$I(q) = \frac{2\pi (\Delta\rho)^2}{q^4} \frac{S}{V} + I_{inc}$$

where $I(q)$ is the differential scattering cross section, $\Delta\rho$ is the difference in scattering length density between the matrix and the scattering feature, S/V is the total surface area per unit sample volume of scatterers, and R is the radius of the scattering feature. A plot of $q^4 I$ vs q^4 should yield a straight line with intercept equal to a known constant times S/V and slope equal to I_{inc} . Figure 1 shows that the Cu scattering data obey a Porod law very well. Figure 2 is a plot of $\ln I$ vs $\ln q$ for the n-Pd data after the incoherent background has been subtracted. The sample compacted at room temperature and annealed at 800° shows a slope of -4 over the entire q range measured. Both the sample compacted at room temperature but given no heat treatment and the sample compacted at 100° have slopes of -4 at higher q values. The low- q scattering is greatly reduced in the 100°C

compacted sample, indicating a lower density of larger defects (microcracks). The sample compacted at 300°C shows no Porod behavior. It is possible that the pores have become so small that other defect features, with a q^{-3} dependence, dominate the scattering.

Figure 3 shows the good agreement that is found between the densities as determined by SANS and by Archimedes principle, for both n-Cu and n-Pd. (The volume fraction of pores estimated by SANS is consistently a little lower than that from Archimedes, probably because very large pores disappear behind the beam stop and are not observed by SANS.) Increasing the compaction temperature from 100 to 300° C produced a significant increase in the density of the Pd samples. The compaction temperatures used for the Cu appear to have been too low to produce such large improvements. The SANS data were interpreted as indicating the presence of voids about the same size as the grains. These are the "missing grain" voids found in the first SANS tests [3], as well as by positron lifetime measurements [1]. As shown in Figure 4 the removal of most of the hydrogen, whether as hydrogen gas or water vapor, strongly affects the influence of temperature on void size. When the gas is present, heating causes both the voids and the grains to grow, but in the samples with diminished hydrogen concentration the voids shrink dramatically. Decrease in void size with increasing compaction temperature is expected if the surface energy forces that cause void shrinkage are not counteracted by a stabilizing gas. (The void size for the 300° compaction sample is not shown, since this sample did not exhibit Porod behavior and it is believed that some other defect dominated the scattering. The arrow in Figure 4 that slopes downwards symbolizes the drop in void size with increasing compaction temperature.) A few measurements of the oxygen content by fast gamma activation analysis (FGAA) were carried out at the University of Kentucky. The results are inconclusive as to a relationship to the hydrogen content. Preliminary data indicate a sub-

stantial increase in the hardness and increase in density in n-Pd with removal of hydrogen.

A brief account of this work will appear as an MRS Conference Proceedings paper from the Spring 1994 meeting, session on Molecularly Designed Ultrafine/Nanostructural Materials. (A copy is attached.) A longer paper, combining these and other results, is in preparation. Further neutron experiments are awaiting the completion of upgrading at the NIST facility. A description of the first SANS experiment appeared in the NIST publication on the Cold Neutron Research Facility. A copy is attached.

A few of the samples were sent to Risø Laboratories in Denmark, where Dr. Morten Eldrup carried out positron lifetime experiments. Like Schaefer [1], Eldrup observed lifetimes corresponding to defects a little smaller than a vacancy and ascribed to trapping at grain boundaries, and a slightly larger pore (about the size of 10 vacancies) that corresponds to Schaefer's "nanovoids" at triple junctions. Eldrup also observed a small signal from a larger size cluster that can be identified with the "missing grain" voids. Further tests, with longer counting times to obtain information on the missing grain voids, is planned when new samples are available.

Synthesis of Nanocrystalline Materials

The new compaction unit has been finished and is working well. This equipment services both the resistively heated inert gas condensation unit and the e-beam unit. It provides dynamic pumping during operation and allows heating of the powder before and/or during compaction. Some of the results (improved density, ability to desorb gases from the powder, higher hardness) obtained by using these features have been described in the previous section.

Production of an alloy, Cu-SiO₂, has been slowed by a series of vacuum leaks in the e-beam equipment. Nevertheless, several

samples have been made and chemically analyzed. They contain around 4-5 at.% Si and about twice as much oxygen, as measured by EDS. Thus the synthesis technique appears to work. Reconstruction of a major source of the leaks, the lens can inside the chamber, is under way. It is expected that the vacuum problem will soon be solved and n-alloy synthesis can be resumed.

Modulus Measurements of Nanocrystalline Iron

A large number of nanocrystalline iron samples were made and their density, grain size and hardness measured. The reactivity of Fe makes it is difficult to establish correlations among these variables, probably because of contamination on the cluster surfaces that ends up at the grain boundaries of the compacted samples. The samples are too brittle for tensile testing. In order to obtain more mechanical information about the nanocrystalline iron than just a microhardness value, the samples were taken by Gretchen Fougere, the graduate student working on this project, to Oak Ridge National Laboratory to use a nanoindenter there, as well as to take pictures of the samples using the Lab's FE-SEM. Figure 5 shows data of elastic modulus versus porosity for various n-iron samples. Results from the literature are included for modulus measurements of several forms of porous coarse-grained iron material. The various curves correspond to predictions of the effect of porosity on modulus. The solid lines are from the work of Krstic et al. [4], and show the drop in modulus expected from spherical pores ($S/R = 0$) or from the opening of cracks around pores under a tensile stress ($S/R = 1$). The dotted line comes from the work of Boccaccini et al. [5], in which it is assumed that the pores are somewhat elongated and are aligned. It can be seen that the modulus of the nanocrystalline iron does not differ significantly from that of coarse-grained iron with comparable porosity. (The three points for n-iron samples that apparently have exceptionally high modulus values

are believed to be in error. It has been found that when the hardness of a sample is very high, as is the case for these three samples, the nanoindenter seriously overestimates the modulus [6].) These results show that the lower modulus values that have been observed in nanocrystalline material are a consequence of the samples not being fully dense, rather than stemming from some esoteric feature such as wide, less dense grain boundaries.

The nanoindenter data are still being analyzed to obtain additional information on the mechanical behavior of the nanocrystalline iron.

Pictures taken by the FE-SEM (Fig. 6) show sharp boundaries between clusters of grains that are less clearly separated. It is possible that these are high angle and low angle boundaries, respectively. The sizes of the grains are roughly comparable to the X-ray values.

Detailed X-ray Measurements of Grain Size, Twins, and Faults

Paul Sanders, the graduate student who has been working with pure Cu and Pd, has carried out a detailed examination of grain size in n-Pd as determined by X-ray line broadening. In particular he has used the Warren-Averbach double peak method [7] to gain information on the grain size as a whole, and the size of sub-units bounded by twin boundaries and stacking faults as well as by grain boundaries. Table II shows the results for n-Pd. The second and third columns show the subunit grain sizes obtained from 111-222 and from 220-400 peaks. If twin boundaries and stacking faults are not considered, the size of grains bounded just by grain boundaries is given in the fourth column. These values are remarkably similar to the results from the Scherrer method using a 200 peak. The probability of a (111) plane being a twin boundary is given by $1/\beta$; of containing a stacking fault is $1/\alpha$. The agreement between the last two columns, one obtained from measured peak shifts and peak asymmetries, the other from

Warren-Averbach calculations, serves as an indicator of the reliability of the calculations. On the whole the agreement is very satisfactory. Measurements on n-Cu will be carried out next. Copper has a lower SFE than palladium, and therefore should contain more twins and stacking faults. It is planned to compare TEM measurements with the X-ray calculations.

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2. G. Porod, in "Small Angle X-ray Scattering", ed. O. Glatter and O. Kratky, Academic Press, London, 1982, pp 17-51.
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PLANS FOR THE BALANCE OF THE GRANT YEAR

An undergraduate student has been working in the lab this summer (supported by an NSF-MRL program on research experience for undergraduates) to rewrite the program on our miniaturized test machine so that it will do tensile-tensile fatigue. This activity is complete and verification on large grain samples is beginning. Testing also is beginning on the creep equipment

designed for nanocrystalline samples. Paul Sanders, who is carrying out the creep, fatigue, and tensile testing of pure elements, also plans to complete his X-ray studies (mentioned in the Progress Report section) by examining nanocrystalline Cu. The X-ray results on grain size and size of crystallites that are free of twins and stacking faults, will be checked against TEM measurements.

Sample synthesis has been a continuing problem. While the new compaction unit works well, both the resistively-heated and the e-beam evaporation chambers suffer from leaks that lead to oxygen and other contaminant levels that degrade mechanical properties of the nanocrystalline samples. Funding has been obtained from Argonne National Lab (with a small contribution from this grant) to rebuild the old resistively-heated chamber. Paul Sanders, working with Dr. Jeff Eastman of Argonne, has designed and is building the new unit. This process is well underway, and Cu and Pd samples with substantially lower contamination should be available soon. We also are planning to rebuild a part of the e-beam chamber that is subject to a seemingly endless series of leaks. This is essential for the alloy synthesis, being carried out by Carl Youngdahl.

We are expecting Dr. Ruslan Valiev from the Institute of Metals Superplasticity at Ufa, Russia, to be spending two months with our research group this fall. He will be conducting experiments on his iron samples with submicron grain size that are made by intense straining. His stay is being funded by an NRC-COBASE grant.

STATEMENT OF EFFORT

The Principal Investigator is devoting 15% of her effort during the academic year to this project. During the summer 25% of her time is being devoted to it.

Gretchen Fougere has finished her fourth year of graduate

school and is completing her thesis write up. She is working on nanocrystalline iron. She was largely supported by Argonne National Lab. She has taken a job with Motorola. At the Spring 1994 Meeting of the Materials Research Society in San Francisco she won an MRS Graduate Student Award for the presentation of her work on nanocrystalline iron.

Carl Youngdahl and Paul Sanders have finished their third year of graduate school. Carl is working on nanocrystalline composites and Paul on pure metals. Both are examining mechanical behavior and characterizing the internal structure of their materials, and attempting to relate strength to structure, especially defect structure. Mechanisms of deformation are of special interest.

In this work we are collaborating with Drs. Richard Siegel and Jeff Eastman at Argonne National Laboratory, Professor Heinrich Jaeger at the University of Chicago, Dr. John Barker at NIST, Dr. Victor Tennery at ORNL, Dr. Morten Eldrup at Risø Laboratory, and Professor Ruslan Valiev, Ufa, Russia.

PAPERS AND ORAL PRESENTATIONS DURING REPORT PERIOD

Papers Published

"SANS and TEM Studies of Isothermal M_2C Carbide Precipitation in Ultrahigh Strength AF1410 Steels", A. J. Allen, D. Gavillet and J. R. Weertman, Acta Metall. Mater. 42 (1993) 1869.

"Small Angle Neutron Scattering from Nanocrystalline Palladium as a Function of Annealing", P. G. Sanders, J. R. Weertman, J. G. Barker and R. W. Siegel, Scripta Metall. Mater. 29 (1993) 91.

"Hall-Petch Behavior of Nanocrystalline Metals", J. R. Weertman, M. Niedzielka and C. Youngdahl, M.A. Nastasi et al. Eds., Kluwer

Academic Press, Dordrecht, The Netherlands, 1993, pp 241-254.

"Hall-Petch Strengthening in Nanocrystalline Metals", J. R. Weertman, Materials Science and Engineering A166 (1993) 161; also in Grain Boundary and Interface Phenomena in the High Temperature Plasticity of Solids, M. E. Kassner and T. G. Langdon, Eds., Elsevier, New York, 1993, pp. 161-68.

"Plastic Deformation of Nanocrystalline Metals", J. R. Weertman and P. G. Sanders, Solid State Phenomena 35-36 (1994) 249.

"On the Hardening and Softening of Nanocrystalline Materials", G. E. Fougere, J. R. Weertman and R. W. Siegel, Nanostructured Mats. 3 (1993) 379.

In Press

"Small Angle Neutron Scattering From Nanocrystalline Pd and Cu Compacted At Elevated Temperatures", P. G. Sanders, J. R. Weertman, J. G. Barker and R. W. Siegel, MRS Conference Proceedings, Spring Meeting 1994.

Oral Presentations

* "Deformation of Nanocrystalline Metals", Dislocations 93: Microstructures and Physical Properties, Aussois, France, 6 April 1993.

* "Nanostructures I", "Nanostructures II", Summer School on "The Mechanics-Materials Linkage" (Institute of Mechanics and Materials), University of Maryland, College Park, MD, 18, 19 August 1993.

* "Strength and Structure of Nanocrystalline Metals", Workshop

on "Interfaces in Materials--Bridging the Length-Scale Gap (Institute of Mechanics and Materials), La Jolla, CA, 14 September 1993.

* "Characterization of Nanocrystalline Metals", University of California/Irvine, Irvine, CA, 21 January 1994.

* "Characterization of Nanocrystalline Metals", Workshop on "Micromechanics of Small Volumes" (Institute of Mechanics and Materials), La Jolla, CA, 11 February 1994.

* "Overview Talk on Mechanical Properties of Nanocrystalline Metals", Conference on Nanophase Materials, Davos, Switzerland, 15 March 1994.

"Small Angle Neutron Scattering from Nanocrystalline Pd and Cu Compacted at Elevated Temperatures", MRS Spring Meeting, San Francisco, CA, 7 April 1994.

* Invited Talk

Table I. Impurities and Grain Size as a Function of Compaction Temperature

Temp.	at% O	at% H (PGAA)	at% H (SANS)	Grain Size (nm)
Pd 20°C			7.5	5.7 ± 0.5
Pd 100°C	0.8 ± 0.3	4.5 ± 1.3	5.2	6.6 ± 0.5
Pd 300°C		< 2.1	0.4	12 ± 0.6
Pd* 200°C	1.2 ± 0.2	< 1.1		9.2 ± 0.3
Pd† 800°C			0.5	59 ± 5
Cu 20°C			7.7	7.7 ± 0.3
Cu 100°C	4.1 ± 0.5	6.3 ± 0.6	5.7	8.9 ± 0.4
Cu 150°C		4.8 ± 0.9	6.5	11 ± 1

*powder warmed by heat lamp prior to 200°C compaction

†RT compaction followed by 800°C anneal

Table 2. X-ray line broadening due to small grain size, twins, and stacking faults

n-Pd Sample	111-222 WA (nm)	200-400 WA (nm)	No twin&SF WA (nm)	Scherrer 111 (nm)	Scherrer 200 (nm)	Scherrer 200 (nm)	Beta twin prob	1/Beta 1 in	Alpha SF prob	1/Alpha 1 in	1.5 Alpha + Beta (WA)	1.5 Alpha + Beta (WA)
20	7.3	4.8	11.9	17.9	10.8	10.8	0.030	34	0.002	593	0.032	0.048
21	6.7	4.4	11.1	15.9	10.0	10.0	0.025	40	0.006	180	0.033	0.053
22	6.8	5.0	9.3	16.5	10.8	10.8	0.023	43	0.002	415	0.027	0.036
23	9.2	6.6	13.2	22.5	14.9	14.9	0.020	51	0.003	317	0.024	0.029
24	6.3	4.4	9.5	15.1	10.0	10.0	0.037	27	0.006	173	0.046	0.048
25	4.1	3.0	5.9	9.9	6.6	6.6	0.023	44	0.004	232	0.029	0.066

planes is a twin

planes is a SF

Compare agreement in two columns

Fig. 1. Determination of I_{inc} and C_p for n-Cu.

Fig. 2. SANS data for n-Pd.

Fig. 3. Density of n-Pd (a) and n-Cu (b).

Fig. 4. Grain or void diameter in n-Pd (a) and n-Cu (b).

Fig.5. Young's modulus vs volume fraction of porosity for iron. Data points are for nanocrystalline iron (this experiment) and for a variety of coarse-grained porous Fe samples (from the literature). Solid lines are from the work of Krstic et al. [4] for pores with and without associated cracks; dotted lines from Boccaccini et al. [5] for elliptical, oriented pores.

Fig. 6. FE-SEM picture of nanocrystalline iron sample.