CONF-8906247--1

ANF-8906247--1

NANOPHASE MATERIALS ASSEMBLED FROM ATOMIC CLUSTERS*

R. W. Siegel
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

. . .

September 1989

DISCLAIMER

INVITED PAPER to be published in the Proceedings of the International Symposium on Physics of New Materials held in Osaka, Japan on 16 June 1989 to honor the retirement of Professor Francisco Eiichi Fujita from Osaka University.

MASTER

NANOPHASE MATERIALS ASSEMBLED FROM ATOMIC CLUSTERS

R. W. SIEGEL

Materials Science Division

Argonne National Laboratory

Argonne, Illinois 60439 USA

ABSTRACT

The preparation of atomic clusters of metals and ceramics by means of the gas-condensation method, followed by their in situ consolidation under high-vacuum conditions, has recently led to the synthesis of a new class of ultrafine-grained materials for which their physics is intimately coupled with their application. These nanophase materials, with 2 to 20 nm grain sizes, appear to have properties that are often rather different from conventional materials, and also processing characteristics that are greatly improved. The nanophase synthesis method described here should enable the design of materials heretofore unavailable, with improved or unique properties, based upon an understanding of the physics of these new materials.

INTRODUCTION

This paper is dedicated to my friend Professor Francisco Eiichi Fujita on his retirement from Osaka University. Having arrived myself at the University of Illinois at Urbana-Champaign only in September of 1958, I missed meeting Francis Fujita and Uli Gonser until some years later. Although we have not yet participated in research together, I had the distinct honor and pleasure to work together with Francis in organizing a United States-Japan Seminar on Electronic Structure and Lattice Defects in Alloys [1] held in May 1987 at the East-West Center in Honolulu, Hawaii. The subject area of that Seminar has been a thread over the years through the fabric of Fujita-sensei's research, as well as my own. The new subject of nanophase materials, the focus of

my closing talk at our US-Japan Seminar as well as the subject of this Symposium contribution, also embodies such a thread. However, it adds to this thread a recently recognized and developed opportunity for the controlled synthesis of materials. I suspect that the combination of new capabilities to synthesize, characterize, and engineer the properties of materials based upon their physics, via the assembly of atomic clusters or the multilayering of thin films, for example, will revolutionize materials science in the coming years.

The modern synthesis of ultrafine-grained materials by the in situ consolidation of ultrafine particles or atomic clusters was suggested by Gleiter [2], based upon the considerable body of earlier research into the production of ultrafine metal particles by means of the gas-condensation method and the assembled knowledge on powder metallurgy and ceramics. The assembly of matter by the consolidation of gas-condensed atomic clusters, however, is probably almost as old as the universe itself, since this is most likely the manner in which condensed matter formed during the cooling period following the 'big bang', as evidenced by the structure of the earliest meteorites. Research on the gas-condensation method and on the resulting atomic clusters during the 1960's and 1970's in Japan [3], the United States [4], and Denmark [5] defined the various parameters that control the sizes of the clusters formed in the conventional gas-condensation method (primarily type of gas, gas pressure, and evaporation rate) that are used to synthesize nanophase materials.

Using the conventional gas-condensation method, the average cluster diameters presently range between about 5 and 25 nm, yielding nanophase materials with such grain sizes. However, more sophisticated applications of the gas-condensation method have been used by cluster chemists and physicists to produce low yields of even smaller monosized atomic clusters [6] that will likely be available in the future for assembly into nanophase materials as well. While nanophase materials can in principle be metals, ceramics, semiconductors, or composites thereof, and can have or contain phases on a nanometer scale with crystalline, quasicrystalline, or amorphous structures, the research carried out to date has concentrated on single-phase metals and ceramics.

SYNTHESIS OF NANOPHASE MATERIALS

Our apparatus for the synthesis of nanophase materials is comprised of an ultrahigh-vacuum (UHV) system fitted with two resistively-heated evaporation sources, a cluster collection device (liquid-nitrogen filled cold finger) and scraper assembly, and in situ compaction devices for consolidating the powders produced and collected in the chamber. This apparatus is shown schematically in Figure 1. The UHV system is first evacuated by means of a turbomolecular pump to below 10^{-5} Pa and then back-filled with a controlled high-purity gas atmosphere at pressures of about a few hundred Pa. For producing metal powders this is usually an inert gas, such as He, but it can alternatively be a reactive gas or gas mixture if, for example, clusters of a ceramic compound are desired. During evaporation of the starting material (or materials) from which the nanophase material will be synthesized, atoms condense in the supersaturated region close to the source and are transported via convection in the gas to the liquid-nitrogen filled cold finger, where they are collected. The gas type and pressure and the material evaporation rate, which are easily controlled, determine the resulting particle-size distributions [4] in such an apparatus.

The clusters that are collected on the surface of the cold finger form very open, fractal or tree-like structures as seen by transmission electron microscopy. They can be very easily removed from this collection surface by means of a Teflon scraper and collected via a funnel into piston-and-anvil devices (Figure 1) capable of compaction pressures up to about 1-2 GPa, in which the nanophase compacts are formed at room temperature. These pellets are typically about 9 mm in diameter and 0.1 to 0.5 mm thick. The scraping and consolidation is performed under UHV conditions after removal of the inert or reactive gases from the chamber, in order to maximize the cleanliness of the particle surfaces and the interfaces that are subsequently formed, while minimizing any possibility of trapping remnants of these gases in the nanophase compact. The synthesis of nanophase materials from atomic clusters has been described in several papers [7-11].

Some of the advantages of nanophase materials, and the nanophase processing method itself, that should be apparent from the description of the synthesis method are as follows: (1) The ultrafine sizes of the atomic clusters and their surface cleanliness allow conventional restrictions of phase

equilibria and kinetics to be overcome during material synthesis, by the combination of short diffusion distances and high driving forces, as well as uncontaminated grain boundaries. (2) The large fraction of atoms residing in the grain boundaries and interfaces of these materials may allow for new atomic arrangements to be formed in significant volume fractions of material and thus novel materials properties may result. (3) The possibilities for reacting, coating, and mixing in situ various types, sizes, and morphologies of clusters create a significant potential for the synthesis of new multicomponent composites with nanometer-sized microstructures and engineered properties.

Although Joule-heated evaporation sources have been normally used in producing clusters for nanophase materials synthesis, it is expected that sputtering, electron beam [12], or laser ablation [13] methods will give better control of the evaporation parameters. These evaporation methods will allow for the use of refractory or reactive sources for clusters and will be especially useful as one moves toward synthesizing more complex multicomponent nanophase materials in the future. Furthermore, the transport of the condensed atomic clusters via gas convection can be improved upon as well by using instead the motion of a forced gas. Forced gas flow is already used in the more sophisticated cluster synthesis methods [6], and it will, among other advantages, greatly facilitate the collection of larger amounts of material than is normally produced (less than a few hundred milligrams) in the type of apparatus shown in Figure 1.

CLUSTER-ASSEMBLED NANOPHASE MATERIALS

Structure - An important aspect of nanophase materials is the large fraction of their atoms that reside in grain boundaries. In this regard they can be thought of as the three-dimensional analogues of multilayered materials. For example, a nanophase material with a 5 nm average grain size will have from about 30 to 60% of its atoms associated with grain boundaries, taking a grain boundary thickness of about 0.5 to 1.0 nm (ca. 2-4 nearest-neighbor distances). This percentage falls only to about 15-30% for a 10 nm grain size, but is as low as 1-3% for a 100 nm grain size. The properties of these new materials can therefore be expected to be strongly influenced by the defect nature of their internal boundaries and the electronic-structure changes resulting therefrom, simply because of the very large number density of these boundaries.

The structures of nanophase materials, both metals and oxides, have been investigated by a number of direct and indirect methods including transmission electron microscopy, x-ray and neutron scattering, and Mössbauer, Raman, and positron annihilation spectroscopy. It has been found that the grains in nanophase compacts are typically rather equiaxed, as are the clusters from which they were assembled, and retain the narrow log-normal size distributions representative of the clusters formed in the gas-condensation method. Their grain sizes, moreover, remain rather deeply metastable to elevated temperatures, and their grain size distributions appear to scale with their growth, when it occurs. Figure 2 shows a typical grain size distribution for a nanophase sample, in this case TiO_2 with the rutile structure [14]. The 12 nm initial average grain diameter for this distribution changes little with annealing to elevated temperatures until about 40-50% of the sample's absolute melting temperature is reached. This behavior appears to be rather typical for nanophase oxides [11], as shown in Figure 3, and for nanophase metals as well.

Since a large fraction of their atoms reside in the grain boundaries of nanophase materials, the interface structures can play a significant rôle in determining the properties of these materials. A number of investigations on nanocrystalline metals by Gleiter and coworkers [15], including x-ray diffraction, Mössbauer spectroscopy, positron lifetime studies, and most recently EXAFS, have been interpreted in terms of grain boundary atomic structures that may be random, rather than possessing either the short-range or long-range order normally found in the grain boundaries of coarser-grained polycrystalline materials. However, recent investigations of nanophase TiO_2 by Raman spectroscopy [16] and of nanophase palladium by atomic resolution, transmission electron microscopy [17] indicate that the grain boundary structures in these materials are quite normal. The boundaries appear to contain short-range ordered structural units representative of the bulk material and distortions that are localized to about ± 0.2 nm on either side of the grain boundary plane (Figure 4). These latter conclusions would also seem to be consistent with the expectations from condensed matter theory and the known healing distances in these materials.

Positron annihilation spectroscopy has been a useful tool in the study of the inherently ultrafine-scale porosity in nanophase compacts, which can be probed to advantage by PAS as a function of sintering temperature to observe densification. An example of PAS lifetime results [14]

used to follow the sintering behavior of nanophase TiO_2 is shown in Figure 5. The intensity I_2 of the lifetime (τ_2) signal corresponding to positron annihilation from void-trapped states in the nanophase sample is seen to decrease rapidly during sintering above 500°C as a result of the densification of this ultrafine-grained ceramic, even though rapid grain growth does not set in until above 800°C. Furthermore, the variation of τ_2 with sintering indicates that there is a redistribution of void sizes accompanying this densification that can also be followed by PAS. Similar behavior is also observed for the coarser-grained samples. However, as expected, the densification proceeds more slowly in these latter samples and the pore sizes are larger according to the larger values of τ_2. The electronic structure of nanophase materials could be usefully investigated by PAS, particularly that associated with the interface structures in these materials, but such studies have not yet been carried out.

Properties - Nanophase materials have properties that are often considerably improved in comparison with those of conventional structures. For example, nanophase TiO_2 (rutile) exhibits considerable improvements in both the sinterability and resulting mechanical properties of this material relative to conventionally synthesized rutile. Results of microhardness measurements as a function of sintering temperature for nanophase TiO_2 (rutile) with an initial average grain size of 12 nm are compared in Figure 6 with similar measurements on two coarser-grained samples produced from commercial TiO_2 powders ball-milled to 1.3 μm average diameter. The nanophase TiO_2 is seen to sinter at 400 to 600°C lower temperatures than the coarser-grained material, and without the need for the compacting and sintering aid polyvinyl alcohol (pva); without pva the commercial TiO_2 did not effectively sinter. Also, the resulting fracture characteristics [18] developed for the nanophase TiO_2 were better than those for conventional rutile. It may not be terribly surprising that nanophase ceramics, with their ultrafine grain sizes, clean cluster surfaces, and high grain boundary purity, will sinter at much lower temperatures than conventional coarser-grained ceramics. However, it is unique that they can also retain their fine grain sizes after sintering to full density and exhibit superior mechanical properties as well.

Beyond their enhanced sinterability, the formability of nanophase ceramics is a further distinct advantage to these ultrafine-grained materials. This formability is clearly evident in the sample

compaction process [14] and it has been demonstrated through deformation [19] as well. The degree to which nanophase ceramics are truly ductile is only beginning to be understood. Nanoindenter measurements [20] on nanophase TiO_2 have recently demonstrated that a dramatic increase of strain rate sensitivity occurs with decreasing grain size, as shown in Figure 7. The strain rate sensitivity values at the smallest grain size yet investigated (12 nm) indicate ductile behavior of this ceramic, as well as a significant potential for increased ductility at even smaller grain sizes. However, no superplasticity has yet been observed in these materials.

While the microhardness of as-compacted nanophase oxides is reduced relative to their fully dense counterparts, owing to significant porosity in addition to their ultrafine grain sizes, the case for nanophase metals is quite different. Figure 8 shows recent microhardness results for nanophase palladium and coarser-grained samples as a function of annealing [21]. In the as-compacted state, the nanophase palladium samples with 5-10 nm grain sizes exhibit a four-fold increase in hardness over the coarser-grained (ca. 100 μm) samples. Up to about 50% of the absolute melting temperature, the hardness falls only slowly with annealing, commensurate with the rather deep observed grain size metastability in these materials cited earlier. The increased hardness in these ultrafine grain size metals, which is supported by yield stress measurements as well, seems at least analogous to the Hall-Petch strengthening observed in coarser-grained metals, but the responsible defect mechanisms may need to be accommodated to the grain-size scale in these materials.

The atomic diffusion behavior in nanophase materials, which may have a significant bearing on their mechanical properties such as creep at elevated temperatures, has been found to be quite interesting. Measurements of self-diffusion and impurity-diffusion [22, 23] in as-compacted nanocrystalline metals and ceramics indicate that atomic transport is orders of magnitude faster in these materials than in coarser-grained polycrystalline samples. This rapid diffusion appears to be intrinsically coupled with the porous nature of the interfaces in these materials, and can be suppressed back to conventional values by sintering to full densities. Nonetheless, there seem to exist considerable possibilities for efficiently doping nanophase materials via the rapid diffusion available along their ubiquitous grain-boundary networks to synthesize materials with tailored optical, electrical, or mechanical properties.

CONSIDERING THE FUTURE

We are only beginning to take advantage of the opportunities for synthesizing nanophase materials via the assembly of atomic clusters. The future appears to hold great promise for these materials, based upon the limited knowledge that has already been accumulated. The cluster sizes accessed to date indicate that the high reactivities and short diffusion distances available in cluster-assembled materials can have profound effects upon the processing characteristics of these materials. These characteristics should be further enhanced as even smaller and more uniformly sized clusters become available in sufficiently large numbers to effect their assembly into usable materials. In addition, the enhanced diffusivities along their grain boundary networks, with only few atomic jumps separating grain interiors from grain boundaries, should enable efficient impurity doping of these materials. Nanophase insulators and semiconductors, for example, could be easily doped with impurities at relatively low temperatures allowing efficient introduction of impurity levels into their band gaps and control over their electrical and optical properties. Moreover, the ability to produce via cluster assembly fully dense ultrafine-grained nanophase ceramics that are formable and exhibit ductility can have a significant technological impact in a wide variety of applications. Subsequent controlled grain growth can then be used to alter the properties of these ceramics.

Research on cluster-assembled nanophase materials is currently being carried out in only a few laboratories, and much work still remains to be done. Nevertheless, it can be expected that an understanding of the essential defect nature of these interfacial materials will be developed in the near future and that the relationships between their atomic and electronic structures and properties will become clear. In order to develop such an understanding, however, a number of aspects regarding nanophase materials need to be elucidated. Primary among these aspects is the characterization of the local structure of the grain boundaries and interfaces in these materials, which comprise such a large fraction of their volumes and affect their properties so dramatically. Much progress has been made in this area recently, but further work is still needed to fully understand which interface characteristics and properties are specific to those in nanophase materials and which are simply representative of interfaces in general and only observable in nanophase materials owing to the uniquely large volume fraction of material that they command.

In addition to further research on the synthesis of a broader range of nanophase materials, encompassing metals, alloys, ceramics, semiconductors, and composites, and the investigations of their structure that will need to accompany such research, measurements of the electrical, optical, magnetic, and mechanical properties of these new materials are certainly needed. A knowledge of the variation of such properties with the detailed structures and synthesis parameters of a variety of nanophase materials should eventually lead to an understanding of the physics of these new materials and consequently to the realization of their full technological potential in the future.

Finally, as I consider the future and Francis Fujita's retirement, I recall a quote from a story by Yukio Mishima set on Uta-Jima in the Gulf of Ise, located about half way as the hawk flies from Osaka to Shizuoka.

> "A hawk was circling in the bright sky over the sea.
> High in the heavens, the hawk was dipping now one
> wing and then the other, as though testing them, and,
> just when it seemed about to plummet downward,
> instead it suddenly slipped backward on the air, and
> then soared upward again on motionless wings."
>
> *The Sound of Waves (Shiosai)*

And so it seems with retiring Japanese professors. While elsewhere, retirement most often signifies the beginning of a downward spiral toward tranquility, I suspect that retirement for Francis Fujita, as with others of my recently retired Japanese friends, represents simply the beginning of another soaring period in his career and life. It is with this expectation that I, joined by my wife Pam, extend our best and warmest wishes for the future to Francis, his wife Yoko, and their lovely family.

REFERENCES

1. R. W. Siegel and F. E. Fujita, eds., **Electronic Structure and Lattice Defects in Alloys**, Mater. Sci. Forum 37 (Trans Tech Publ., Aedermannsdorf, 1989)

2. H. Gleiter, in **Deformation of Polycrystals: Mechanisms and Microstructures**, N. Hansen et al., eds. (Risø National Laboratory, Roskilde, 1981) p. 15.

3. K. Kimoto, Y. Kamiya, M. Nonoyama, and R. Uyeda, Jpn. J. Appl. Phys. 2, 702 (1963).

4. C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. 47, 2200 (1976).

5. A. R. Thölén, Acta Metall. 27, 1765 (1979).

6. R. P. Andres, R. S. Averback, W. L. Brown, L. E. Brus, W. A. Goddard, III, A. Kaldor, S. G. Louie, M. Moskovits, P. S. Peercy, S. J. Riley, R. W. Siegel, F. Spaepen, and Y. Wang, J. Mater. Res. 4, 704 (1989).

7. R. Birringer, U. Herr, and H. Gleiter, Suppl. Trans. Jpn. Inst. Met. 27, 43 (1986).

8. R. W. Siegel and H. Hahn, in **Current Trends in the Physics of Materials**, M. Yussouff, ed. (World Scientific Publ. Co., Singapore, 1987) p. 403.

9. H. Hahn, J. A. Eastman, and R. W. Siegel, in Ceramic Transactions, **Ceramic Powder Science**, Vol. 1, Part B, G. L. Messing et al., eds. (American Ceramic Society, Westerville, 1988) p. 1115.

10. R. W. Siegel and J. A. Eastman, Mater. Res. Soc. Symp. Proc. 132, 3 (1989).

11. J. A. Eastman, Y. X. Liao, A. Narayanasamy, and R. W. Siegel, Mater. Res. Soc. Symp. Proc. 155, 255 (1989).

12. S. Iwama, K. Hayakawa, and T. Arizumi, J. Cryst. Growth 56, 265 (1982).

13. A. Matsunawa and S. Katayama, in **Laser Welding, Machining and Materials Processing**, Proc. ICALEO '85, C. Albright, ed. (IFS Publ. Ltd.,1985).

14. R. W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu, and R. Gronsky, J. Mater. Res. 3, 1367 (1988).

15. R. Birringer and H. Gleiter, in **Encyclopedia of Materials Science and Engineering**, Suppl. Vol. 1, R. W. Cahn, ed. (Pergamon Press, Oxford, 1988) p. 339.

16. C. A. Melendres, A. Narayanasamy, V. A. Maroni, and R. W. Siegel, J. Mater. Res. 4, 1246 (1989).

17. G. J. Thomas, R. W. Siegel, and J. A. Eastman, Mater. Res. Soc. Symp. Proc. 153, 13 (1989).

18. Z. Li, S. Ramasamy, H. Hahn, and R. W. Siegel, Mater. Lett. 6, 195 (1988).

19. J. Karch, R. Birringer, and H. Gleiter, Nature 330, 556 (1987).

20. M. J. Mayo, R. W. Siegel, A. Narayanasamy, and W. D. Nix, J. Mater. Res., to be published (1989).

21. G. W. Nieman, J. R. Weertman, and R. W. Siegel, Scripta. Metall., to be published (1989).

22. J. Horváth, R. Birringer, and H. Gleiter, Solid State Commun. 62, 319 (1987).

23. H. Hahn, H.-J. Höfler, and R. S. Averback, Mater. Sci. Forum, to be published (1989).

FIGURE CAPTIONS

Figure 1. Schematic drawing of a gas-condensation chamber for the synthesis of nanophase materials. The material evaporated from sources A and/or B condenses in the gas and is transported via convection to the liquid-nitrogen filled cold finger. The powders are subsequently scraped from the cold finger, collected via the funnel, and consolidated first in the low-pressure compaction device and then in the high-pressure compaction device, all in vacuum. From [10].

Figure 2. Grain size distribution for a nanophase TiO_2 (rutile) sample compacted to 1.4 GPa at room temperature, as determined by transmission electron microscopy. From [14].

Figure 3. Variation of the average grain size, measured by dark-field transmission electron microscopy, with sintering temperature for nanophase TiO_2, MgO/WO_x, and ZnO. The samples were annealed for one-half hour in air at each temperature. From [11].

Figure 4. High resolution transmission electron micrograph of a typical grain boundary in nanophase palladium. The magnification is indicated by the lattice fringe spacings, which are 0.195 nm ({002} planes) or 0.225 nm ({111} planes). From [17].

Figure 5. Results of two-component lifetime fits to positron annihilation data from three samples as a function of sintering temperature. A 12 nm, 1.4 GPa nanophase sample (filled circles) is compared to 1.3 μm, 1.4 GPa (open circles) and 1.3 μm, 0.32 GPa (triangles) samples compacted from commercial powder. The PAS data were taken at room temperature; no sintering aids were used. From [14].

Figure 6. Vickers microhardness of TiO_2 (rutile) measured at room temperature as a function of one-half hour sintering at successively increased temperatures. Results for a nanophase sample (squares) with an initial average grain size of 12nm compacted at 1.4 GPa are compared with those for coarser-grained compacts with 1.3 μm initial average grain size sintered with the aid of polyvinyl alcohol from commercial powder compacted at 0.1 GPa (diamonds) and 1.4 GPa (crosses). From [14].

Figure 7. Strain rate sensitivity of nanophase TiO_2 as a function of its grain size. The strain rate sensitivity was measured by a nanoindentation method and the grain size was determined by dark-field transmission electron microscopy. From [20].

Figure 8. Microhardness of three nanocrystalline palladium samples and two coarse-grained palladium samples as a function of annealing temperature. All samples were annealed for 100 minutes in 0.16 Pa vacuum and measured subsequently at room temperature. From [21].
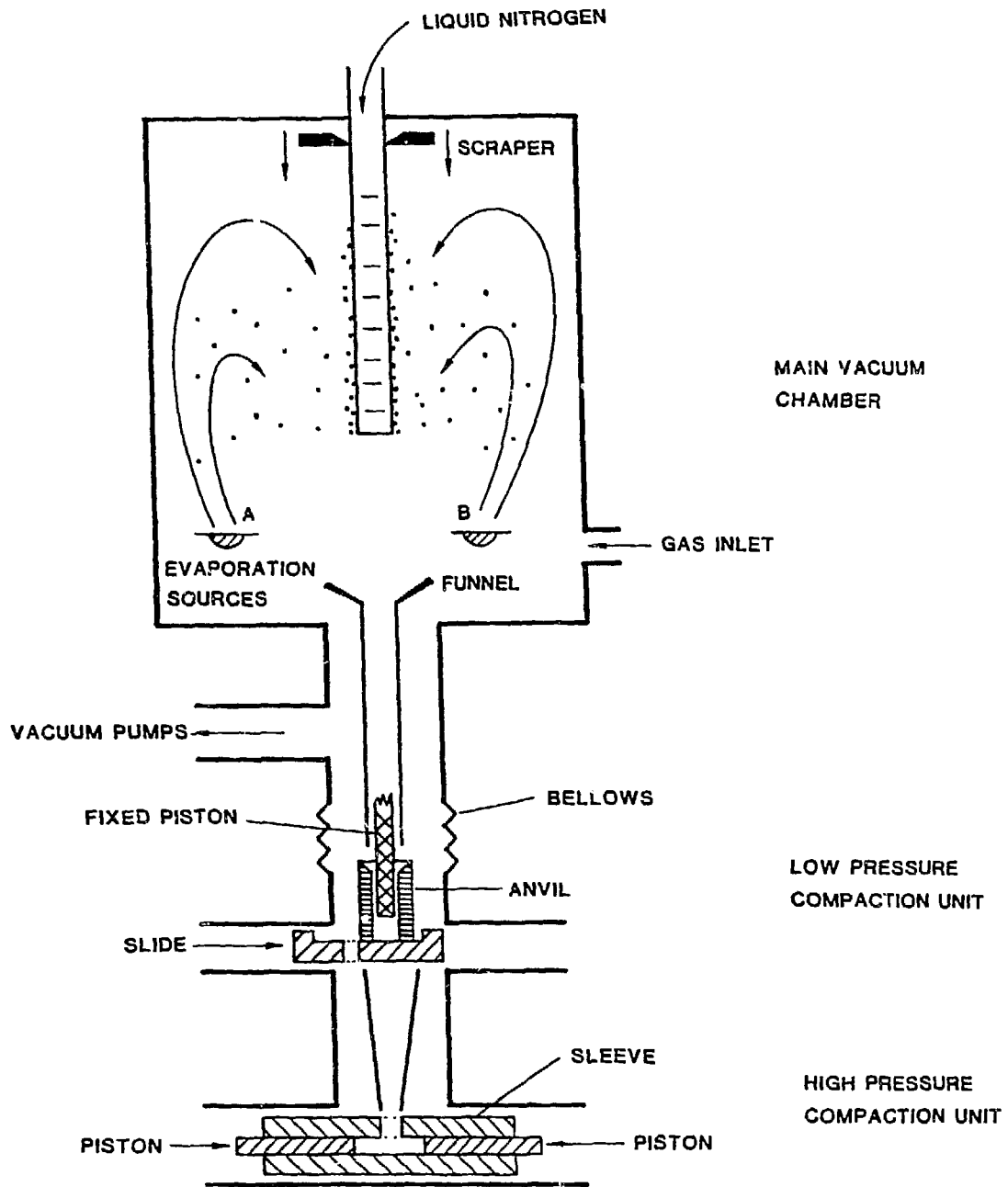
LIQUID NITROGEN

SCRAPER

MAIN VACUUM
CHAMBER

A   B

GAS INLET

EVAPORATION
SOURCES   FUNNEL

VACUUM PUMPS

FIXED PISTON   BELLOWS

ANVIL   LOW PRESSURE
COMPACTION UNIT

SLIDE

SLEEVE

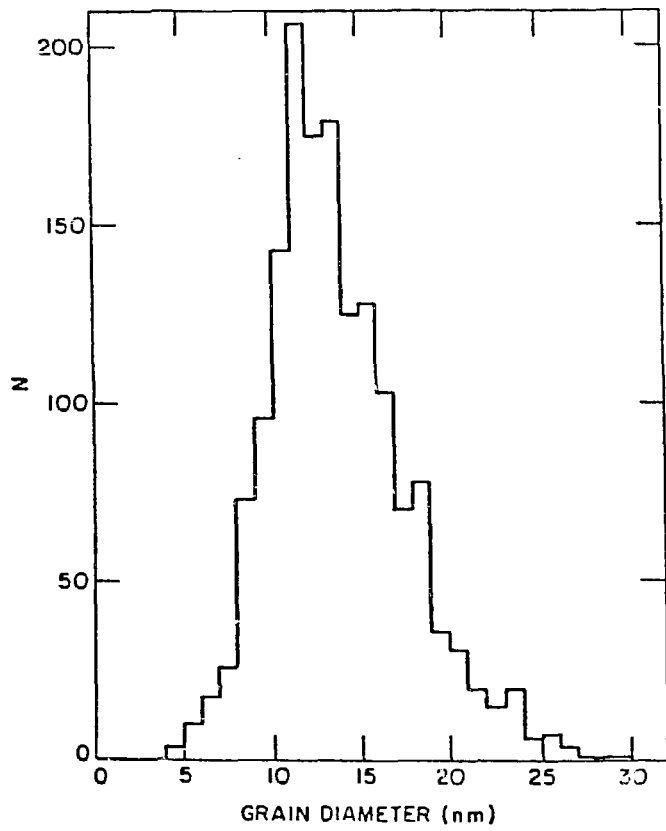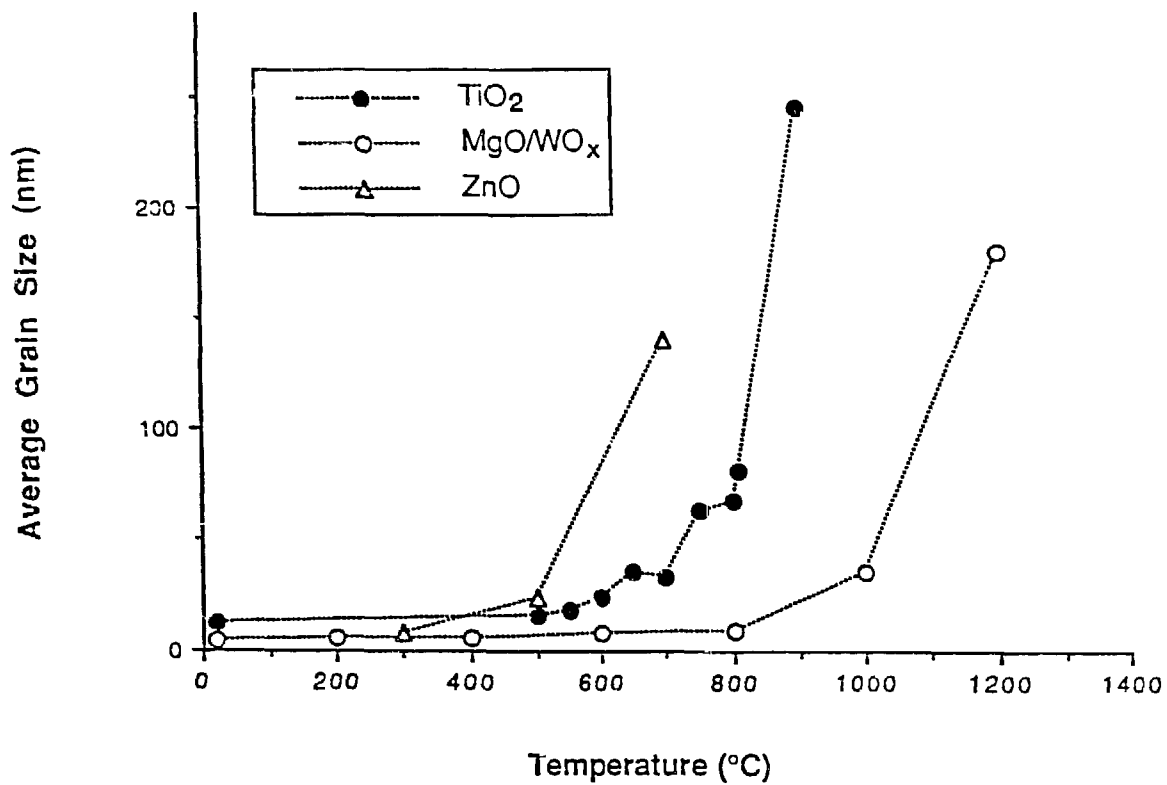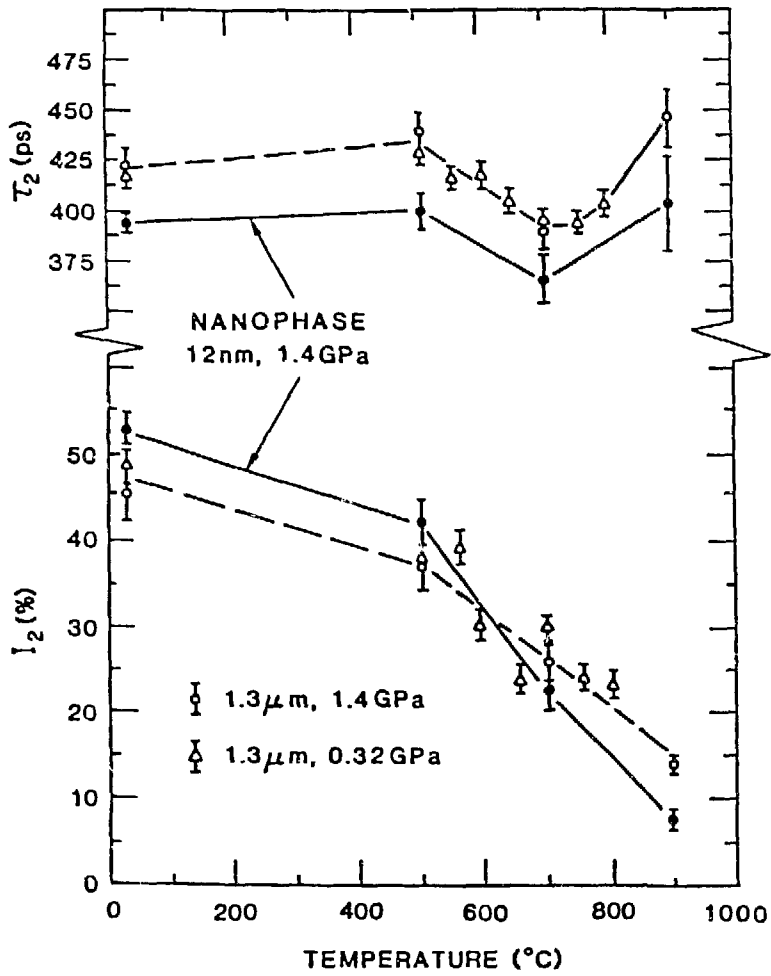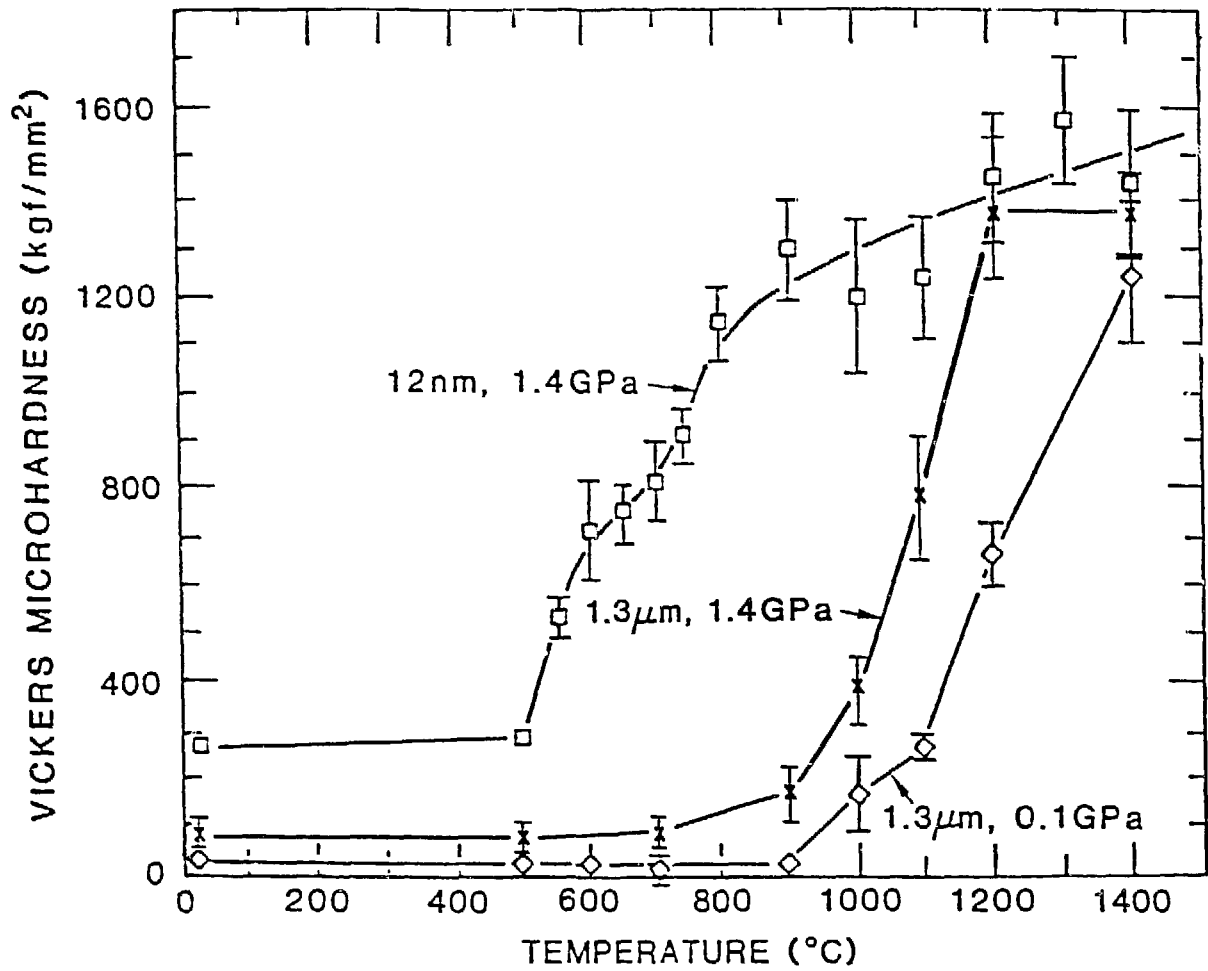HIGH PRESSURE
COMPACTION UNIT

PISTON   PISTON

Figure 1.

GRAIN DIAMETER (nm)

Figure 2.

Figure 3.

Figure 4.

Figure 5

Figure 6.

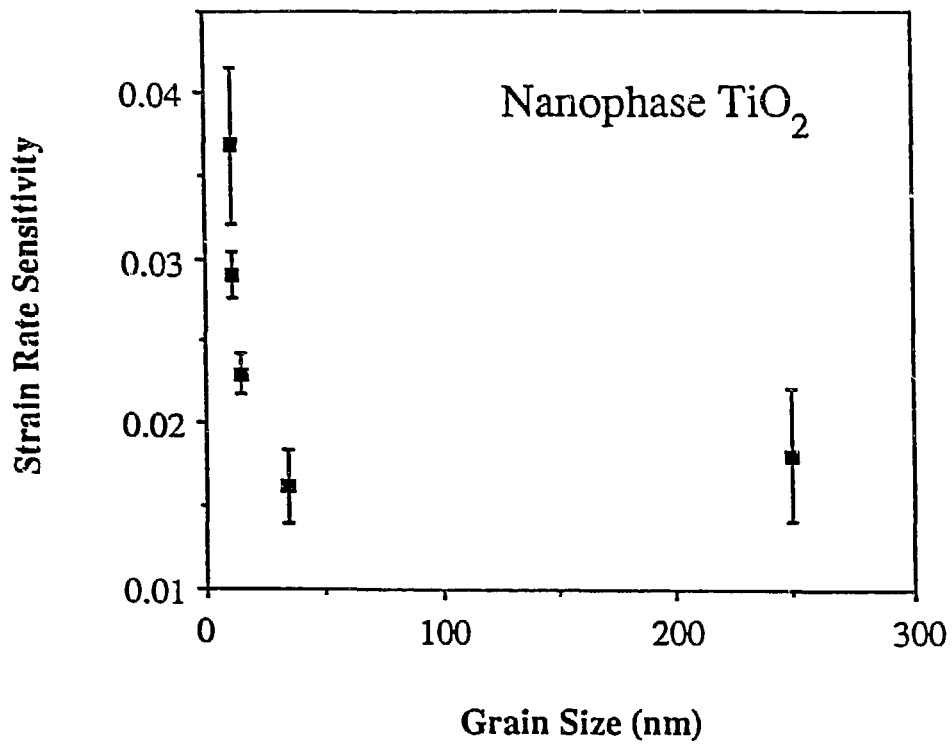Nanophase TiO$_2$

Figure 7.

Figure 8.