



W. G. J. Bunk (Editor)

Advanced Structural and Functional Materials

Proceedings of an International Seminar
Organized by Deutsche Forschungsanstalt
für Luft- und Raumfahrt (DLR), Köln, June 1991

With 101 Figures

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo
Hong Kong Barcelona Budapest

Prof. Dr. Wolfgang G. J. Bunk

Institut für Werkstoff-Forschung

DLR

Postfach 90 60 58

W-5000 Köln 90

ISBN 978-3-642-49263-1

ISBN 978-3-642-49261-7 (eBook)

DOI 10.1007/978-3-642-49261-7

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provision of the German Copyright Law of September 9, 1965, in its current version and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin, Heidelberg 1991

Softcover reprint of the hardcover 1st edition 1991

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Camera ready by authors

61/3020-543210 - Printed on acid-free paper

Foreword

Engineering materials are mainly used for structures. Therefore high-strength, stiffness and sufficient toughness are of prime importance.

For a long time engineers thought first in terms of metals. Material scientists developed alloys tailored to the needs of industry.

Ceramics are known to be brittle and therefore not suitable in the first place for structural application under stress.

Polymers with their low modulus became attractive when reinforced with high-strength fibres. Composites processed by polymer, metal or ceramic matrices and high-strength reinforcements have been introduced into many sectors of industry.

Engineering materials for structural applications fulfil a function: they withstand high stresses, temperatures, fatigue, creep etc. But usually we do not call them functional materials.

Functional materials serve applications apart from classical engineering fields. Electricity conducting materials, semi-conductors, memory alloys and others are called functional materials. Both categories of materials - structural and functional - cover the aspects of the DLR-Seminar 1991 on

"Advanced structural and functional materials".

The seminar is focused on advanced materials in research and development or at the edge of being introduced into the market. Preference was given to materials with a dual character: structural and functional, some of them more structural, some more functional in their potential.

It was necessary to select typical and representative families of materials during the years by R + D activities somewhat matured materials. It was not intended to cover all possible innovations in a two half-days seminar.

The main purpose of the seminar is to bring modern ideas and techniques of engineering science to the attention of DLR scientists and engineers as well as colleagues from industry and academia of many different disciplines in order to stimulate progress in the aerospace market and beyond. The seminar should be an opportunity for learning and understanding the big potential of advanced structural and functional materials.

W.G.J. Bunk

Contents

Nanocrystalline Materials Herbert Gleiter, Universität Saarbrücken	1
Ceramics for Structural Purposes Richard Brook, Max-Planck-Institut für Metall- forschung, Stuttgart	39
Thermostructural Ceramic Matrix Composites: An Overview Roger Naslain, Laboratoire des Composites Thermo- structuraux, F-Pessac	51
Intermetallics - Fundamentals and Prospects Hans-Jürgen Engell; Armin von Keitz; Gerhard Sauthoff, Max-Planck-Institut für Eisenforschung, Düsseldorf	91
Shape Memory Alloys Erhard Hornbogen, Ruhr-Universität, Bochum	133
Self-Reinforcing Polymer Composites Gerhard Wegner, Max-Planck-Institut für Polymerfor- schung, Mainz	165
Functional Molecular Materials derived from Organic Conducting Polymers Francis Garnier, Laboratoire des Matériaux Moléculaires, C.N.R.S., F-Thiais	175
Piezoelectric Composites Helmut Thomann, Siemens AG, München	199
Superconducting Materials J. Georg Bednorz, IBM-Forschungslabor, CH-Rüschlikon (not available at the time of printing)	

Nanocrystalline Materials

H. Gleiter

Universität des Saarlandes, Gebäude 43, Institut für Neue
Materialien, 6600 Saarbrücken, Germany

ABSTRACT

Nanocrystalline solids are polycrystals the crystal size of which is a few (typically 1 to 10) nanometers so that 50% or more of the solid consists of incoherent interfaces between crystals of different crystallographic orientations. Materials consisting primarily of internal interfaces represent a separate state of solid matter because the atomic arrangements formed in the cores of interfaces are known to be arrangements of minimum energy in the potentials field of the adjacent crystal lattices. The boundary conditions imposed on the atoms in the interfacial cores by the adjacent crystal lattices, result in atomic structures in the interfacial cores which cannot be formed elsewhere (e.g. in glasses or perfect crystals). Nanocrystalline materials seem to be of interest for the following four reasons:

- (1) Nanocrystalline materials exhibit atomic structures which differ from the two known solid state structures: the crystalline and the glassy state.
- (2) The properties of nanocrystalline materials differ (in some cases by several orders of magnitude) from those of glasses and/or crystals with the same chemical composition.
- (3) Nanocrystalline materials seem to permit the alloying of conventionally insoluble components.
- (4) If small (1 to 10 nm diameter) glassy droplets are consolidated (instead of small crystals), a new type of glasses, called nanoglasses, is obtained. Such glasses seem to differ structurally from glasses generated by rapid solidification.

INTRODUCTION

Research on "Nanocrystalline Materials" has been initiated less than a decade ago. Thus, the term nanocrystalline materials, may not be familiar to all readers. Let us therefore start by addressing the questions:

- (i) What are nanocrystalline materials and(ii) why are they of interest?

Many properties of solids are known to depend on their atomic structure. Hence, if we succeed in generating a solid with a novel atomic structure, this solid is likely to exhibit novel properties as well. As nanocrystalline materials seem to have an atomic structure deviating from the presently available solid state structures (1), they may open the way for generating solids with new properties. The basic reasons suggesting nanocrystalline materials to have a new type of atomic structure are summarized in Figs. 1 and 2. The two figures indicate the atomic arrangements in the vicinity of an edge dislocation in a cubic crystal (Fig. 1) and an incoherent grain boundary between two cubic crystals tilted relative to one another by 36.9° about a common $[100]$ axis (Fig. 2a). The atomic structure of the boundary was deduced from a high resolution electron micrograph (Fig. 2b, section A) of a 36.9° $[100]$ tilt boundary between NiO crystals (Merkle et al 1987). NiO has a NaCl type structure. The cores of both lattice defects exhibit the following two characteristic features. A reduced atomic density and a modified atomic structure in comparison to the perfect lattice. In fact, the core of the edge dislocation may be described in terms of a channel comprising seven atoms in every cubic plane (Fig. 1).

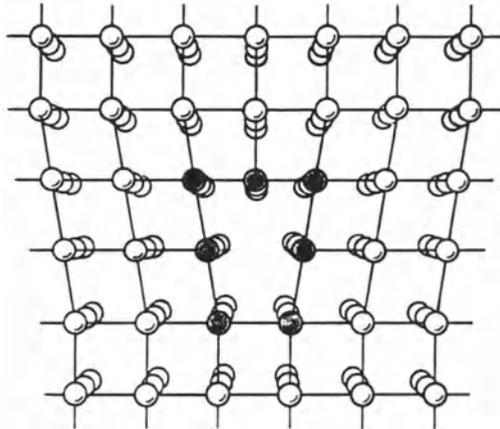


FIG. 1 Edge dislocation in a simple cubic crystal. In the dislocation core, the atomic density and coordination is changed in comparison to the perfect cubic lattice. In fact, the core of the dislocation may be interpreted as a channel formed by seven atoms as indicated in Fig. 1, whereas the crystal has a cubic structure.

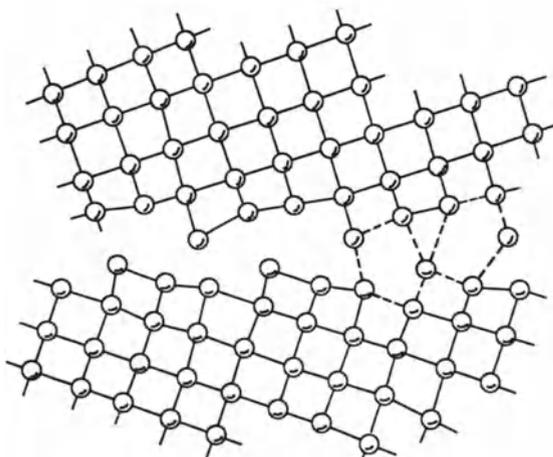


FIG. 2a Atomic structure in the core of grain boundary between two crystals tilted relative to one another by 36.9° about a common $[100]$ direction. The structure was deduced (2) from the high resolution electron micrograph shown in Fig. 2b (section A). The boundary core structure may be described as a two-dimensional periodic array of two different pentagonal polyhedra (indicated on the right side of the boundary).

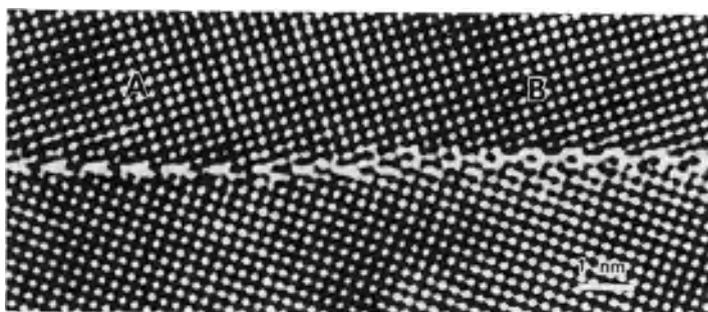


FIG. 2b Electron micrograph of a symmetric 36.9° $[100]$ tilt grain boundary in NiO (2). The black regions represent the atomic positions. In the boundary core the atomic density and coordination is changed in comparison to the perfect lattice. The boundary structures in the facets A and B are different due to the vertical displacement of the boundary plane relative to the two crystals.

The structure of the grain boundary core shown in Fig. 2a represents a periodic sequence of two different pentagonal polyhedral units tilted relative to one another whereas the two crystal lattices have a cubic structure. The newly formed atomic arrangements in the boundary core result in interatomic spacings

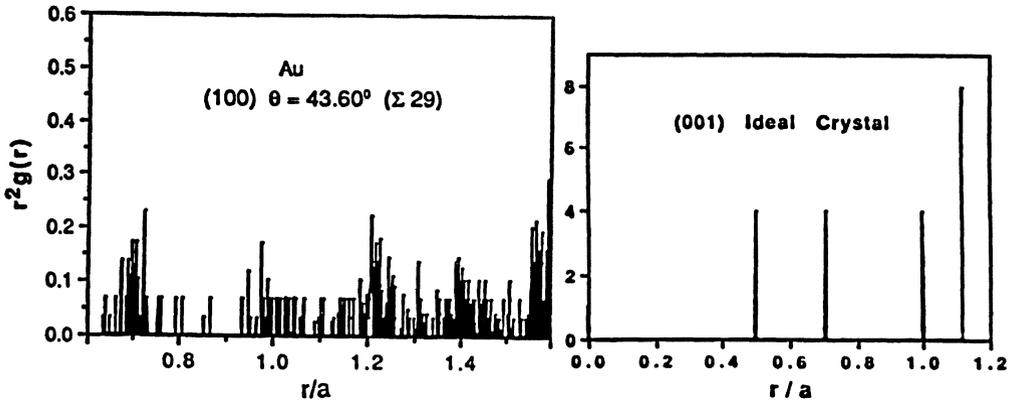


FIG. 2c Radial distribution function, $r^2g(r)$. for the atoms in the core of a 43.6° (100) ($\Sigma 29$) boundary as described by an embedded atom potential for gold (left side). The figure on the right, displays the radial distribution function of an ideal crystal on (001) (80).

that cannot exist in the perfect lattice. For example Fig. 2c displays the distribution of interatomic spacings in the core of a 36.9° [001] boundary in gold in comparison to the spacings in the perfect lattice of the same material. Obviously, the boundary core is characterized by a broad distribution of interatomic spacings and atomic arrangements which cannot be formed in the perfect lattice. The physical reason for the reduced atomic density and the modified atomic arrangements in the boundary cores may be seen by considering, for example, the structure of the grain boundary core shown in Fig. 2a. The boundary core is the region where two crystals with different crystallographic orientations are joined together. Due to the different orientations, the two adjacent crystal lattices match poorly. The poor matching results in an atomic density in the core region which is lower than in the perfect lattice. The

density reduction depends on the crystallographic parameters of the boundary such as the orientation relationship between both crystals, the inclination of the boundary plane relative to both crystal lattices as well as on the interatomic forces i.e. the type of chemical bonding. Typically, the boundary core density is found to be reduced by about 15 to 40% relative to the density of the perfect lattice. In fact, the boundary core density is far lower than in the liquid or glassy state and becomes comparable to the densities of highly compressed gases. The physical reasons for the reduced density and the modified coordination are the constraints exerted by the adjacent crystal lattices on the atoms in the defect cores. Without these constraints the core structures would collapse. In liquids or glasses no constraints of this sort exist and, hence, their structures differ from the one in the cores of defects. There is also another way to see the difference between the structure of the nanocrystalline and the glassy state. In the glassy state, the disorder induced by thermal energy is frozen in. The disorder in nanocrystalline materials results from the incompatibility introduced into the lattice in the form of defects and does not require any thermal energy. Between two given crystals, a large variety of different boundary core structures may be formed because the boundary core structure of a boundary depends on the orientation relationship between both crystals and the boundary inclination. In other words, each time the orientation relationship between both crystals and/or the inclination of the boundary plane is varied, a new boundary core structure with different interatomic spacings (Fig. 2c) is generated.¹ If this is so, then the question arises: Why are these numerous boundary core structures and the reduced density not noticed if we study a polycrystalline solid? If the average crystal size is 10 μm or more, a straightforward estimate indicates that a volume fraction of grain boundary cores in such a polycrystal is less than 10^{-4} , and hence, the atomic arrangements in boundary cores nor-

¹ An example may be seen in Fig. 2b. The boundary plane in section B is displaced relative to A. This displacement results in different boundary core structures in A and B.

mally escape our attention. Nevertheless, precise measurements have revealed the expected effects (3), (4), (5), (77). Thus, if we wish to study and/or utilize the grain boundary core structures, we have to enhance the volume fraction of boundary cores in a polycrystal. This goal may be achieved by reducing the crystal size to a few lattice constants (i.e. a few nanometers) so that the volume fraction of boundary cores approaches 50% or more. If this is done, we obtain solids which consist to a large extent of boundary cores, and hence the atomic structure and the properties of such solids are controlled primarily by the structure and properties of the grain boundary core regions. Solids of this type have been proposed about ten years ago and were called nanocrystalline solids (1), (6) because they are obtained by reducing the crystal size of a polycrystal to a few nanometers. Other terms used in the literature are: ultrafine grained materials, nanophase or nanometer-sized solids. Naturally, they could have equally well be termed "defect core solids". A two-dimensional model of a nanocrystalline material is displayed in Fig. 3. For the sake of clarity, atoms in the various

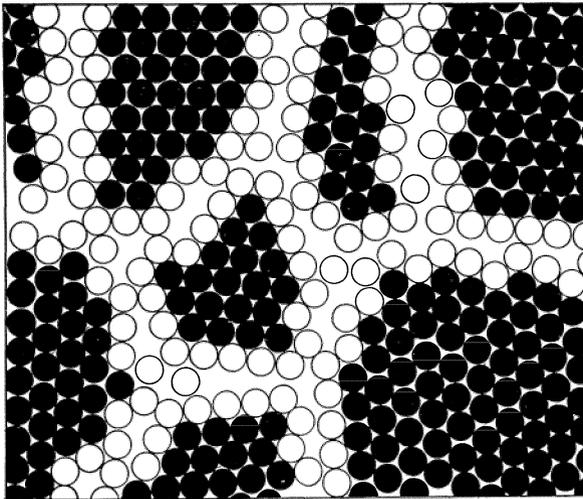


FIG. 3 Atomic structure of a two-dimensional nanocrystalline material. The structure was computed by following the procedure given in ref. 74. The interaction between the atoms was represented by a Morse potential fitted to gold. The atoms in the central portions of the "crystals" are indicated in black. The ones in the boundary core regions are represented by open circles.

crystals are indicated as full circles whereas the atoms in the boundary cores are represented by the open symbols although both types of atoms are assumed to be chemically identical. Structurally, the material consists of the following two components: the crystals with different crystallographic orientations but identical structure and a network of boundaries, the structure of which differs from boundary to boundary and is characterized by the following two features:

- (i) The average atomic density in the boundary regions is about 70% of the crystal density. The boundary density cannot be enhanced by inserting additional atoms because the local free volumes of the vacant sites are too small so that interatomic penetration would result if an atom is inserted.
- (ii) The boundaries exhibit a broad distribution of nearest neighbour configurations and of interatomic spacings ranging from closely packed atoms to widely spaced ones.

In nanocrystalline materials the situation is structurally complimentary to the one in single crystal or a coarse grained polycrystals. In the single crystal or the coarse grained polycrystals, the crystal lattice represents the basic structural component and the lattice defect cores (e.g. dislocation cores, grain boundary cores) are perturbations limited to a small volume fraction of the material. In nanocrystalline materials, the priorities are inverted: the defect cores represent the essential structural component and the residual crystalline regions are required for generating the boundary cores.

In this article we focus attention on the discussion of the basic concepts and features of nanocrystalline materials. The experimental and technical details have been documented in several reviews (7)-(11), (49), (42). As the field finds itself in a state of rapid expansion, many of our present views may have to be modified in the years to come.

HISTORICAL DEVELOPMENT

Although the generation of a new type of solid state structure by utilizing the atomic arrangements in defect cores is less than a decade old, precursor developments can be traced back in history of Materials Science to the turn of this century, and in nature even to the very early state of the universe. The significance of submicroscopic microstructures for mechanical magnetic and electronic properties of solids has apparently been recognized first by Sorby, Tschernoff, Osmond, Howe, Sauveur and others before the turn of the century. Their studies between 1870 and about to 1900 led to the conclusion that the fine-scale microstructure retained after the allotropic transformation of iron alloys gives martensite its hardness. The discovery of precipitation hardening by Wilm in 1906 was the first observation suggesting that the correlation between microstructure and properties (originally proposed for ferrous alloys only) applies to non-ferrous materials as well. Wilm quenched an Al-Cu-Mg-Mn alloy and noticed (after a long weekend) a substantial hardening relative to the as-quenched state. However, it was not until 1919 when Merica, Waltenberg and Scott proposed that the hardening resulted from precipitation of a new phase on a sub-microscopic level. Numerous observations in the subsequent years substantiated and generalized this view and led to the classification of the properties of solids with different types of chemical bonding into structure-sensitive and non-sensitive ones.

In the following years, this classification played an important role in promoting the idea of lattice defects and their significance for crystalline solids. In fact, the physical understanding of the mechanism by which nanometer-sized microstructures affect the properties of solids received a remarkable boost after World War II, from the advent of the theory of lattice defects - in particular dislocation theory - and from the availability of new high resolution research techniques such as electron and field ion microscopy. Both developments elucidated the physical basis for understanding the correlation between the structure-sensitive properties and the microstructure of solids.

As a matter of fact, the development of most high strength and high temperature materials available today is based on the results of those studies. When it was recognized that dislocations play a similar role for the mechanical behaviour of materials as do domain walls or flux lines for ferromagnetic or superconducting properties, respectively, it became apparent that ferromagnetic and superconducting properties can be manipulated, too, by suitably varying the microstructure (12). In fact, the pinning of ferromagnetic domain walls or of flux lines in type II superconductors by finely dispersed precipitates leads to magnetic materials with high coercive forces and superconductors with high critical current densities (12). Instead of reducing the motion of dislocations by precipitates from supersaturated solid solutions, small second phase particles introduced by means of powder metallurgy or by extrusion of two phase coarse-grained structures (13), (14) may be used as well. The enhanced defect density in irradiated, in highly cold worked (15) as well as in fine-grained materials (16) results in similar effects because the defects inhibit dislocation motion. A closely related approach in the field of ceramics generated by the sol-gel method was the proposal, to use heterogeneity on a nanometer scale (17)-(22). This approach was based on the hypothesis that diphasic or multiphasic ("nanocomposit") xerogels which are heterogeneous on a nanometer scale store more energy than a single phase gel and thus exhibit new properties.

About 1970, a second period of developments in the area of nanometer-sized microstructures started when it was recognized that specifically tailored nanometer-sized microstructures permit the generation of solids with new atomic and/or electronic structures. These developments seem to bring Feynman's dream of nanotechnology (23) closer to reality. In the area of semiconducting materials extensive research activities were initiated on a new two-dimensional class of materials with a nanometer-scale microstructure by the proposal of an "engineered" semiconductor superlattice (24), (25) consisting of alternate thin, fully coherent layers with different dopings or different compositions leading to new electronic structures. These superlattices represent an extension of double- or multibarrier structures

where quantum effects prevail because the layers have a thickness of a few lattice constants. Several recent reviews of the present state of understanding of the physics and application of quantum well structures and superlattices have been compiled in ref. (26). The nanocrystalline materials discussed in this paper represent the second example of a tailored nanometer-sized microstructures. Although the characteristic dimension (at least in one direction) are comparable in the case of semiconductor superlattices and nanocrystalline materials, both groups of materials differ in the underlying physical concepts. Semiconductor superlattices are based on quantum size effects due to the small thickness of the layers that are joined together by fully c o h e r e n t interfaces. Incoherent interfaces would be detrimental. In nanocrystalline materials the situation is inverted. It is the peculiar atomic structures formed in the cores of i n c o h e r e n t interfaces (or other defect cores) that are utilized. The small dimensions of the crystals are required to obtain a large volume fraction of incoherent interfaces. However, quantum size effects play no role.

Long before, materials with nanometer-sized microstructures have been synthesized by man, they have been formed in several natural composites. For example, human teeth are an exquisitely tailored composite at the 1-2 nm level of fibrils of hydroxyapatite topotactically grown onto collagen. A similar structure is found in natural corals and in the shells of abalone. Semicrystalline polymers are composed of plate shaped crystalline regions with thicknesses of typically 1-3 nm. The crystalline regions are separated by "amorphous" layers consisting of tie molecules between adjacent crystallites as well as macromolecules folded in a regular or irregular fashion. Probably the oldest solids with a nanometer-sized microstructure are primitive meteorites in which aggregates of carbon atoms or silicon carbide of 5nm or less are found. These aggregates are believed to be formed by condensations in the early age of the solar system or in interstellar space (27), (28). Asbestos, opals and calcedon represent minerals with a nanometer-sized microstructure formed on the surface of the earth many millions years before any man-made substance of this type was available.

The earliest applications of materials with nanometer-sized microstructures have been revealed in ancient Egypt and China where the size of the pigments of certain colours has been reduced into the submicron regime by grinding or milling in order to enhance the intensity of the colours.

PREPARATION

The experimental arrangement used most frequently to prepare nanocrystalline solids is a modified gas condensation method (Fig. 4), where the material (e.g. Fe) is evaporated into an inert gas atmosphere (e.g. He, pressure about 0.1...1 kPa).

Through interatomic collisions with the He atoms, the evaporated Fe atoms lose kinetic energy and condense in the form of small crystals a few nanometers across which accumulate on a vertical cold finger as a loose powder. After restoring high vacuum ($<10^{-6}$ Pa) the powder is stripped off and funneled into a piston and anvil device where it is compacted (pressure up to 5 GPa) into a pellet. Sputtering, electron gun or laser evaporation may be employed instead of thermal evaporation. Other methods which have been utilized to obtain fine grained powders suitable for generating nanocrystalline solids are ball milling (e.g. applied to Ru), vapour phase synthesis, sliding wear, decomposition of suitable compounds and precipitation from solutions or gels. In the latter cases, special care has to be taken to remove surface contaminants. A systematic study of the impurity content of nanocrystalline solids prepared by inert gas condensation revealed that gaseous and metallic impurities were less than 5% and He less than 50 ppm. The density of metallic nanocrystalline materials after consolidation varied between 75% and more than 90% of the crystalline density (depending on the material), approaching 100% after grain growth. The distribution of crystal sizes was determined by transmission electron microscopy and small angle X-ray or neutron scattering. A typical distribution (for nanocrystalline Pd) is presented in Fig. 5. For further details we refer to ref 40.

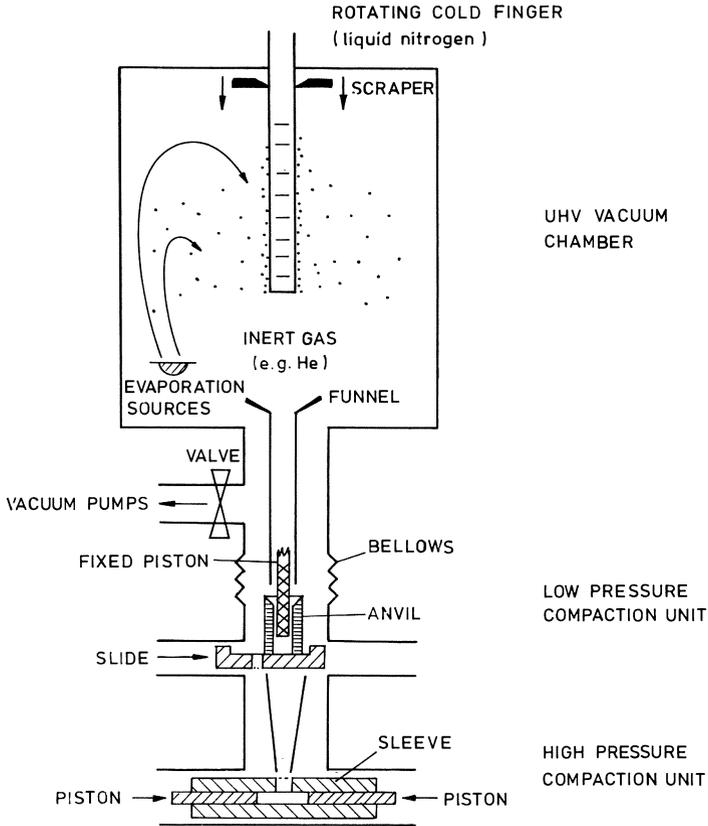


FIG. 4 Schematic drawing of a gas-condensation chamber for the synthesis of nanocrystalline materials. The material evaporated condenses in the inert gas in the form of small crystallites which are subsequently transported via convection to the liquid nitrogen filled cold finger. The powder of crystallites is finally scraped from the cold finger, collected via the funnel and consolidated first in the low-pressure compaction unit and then in the high-pressure compaction unit. Both units are kept under UHV conditions. Instead of an evaporation device, a sputtering source has been utilized successfully.

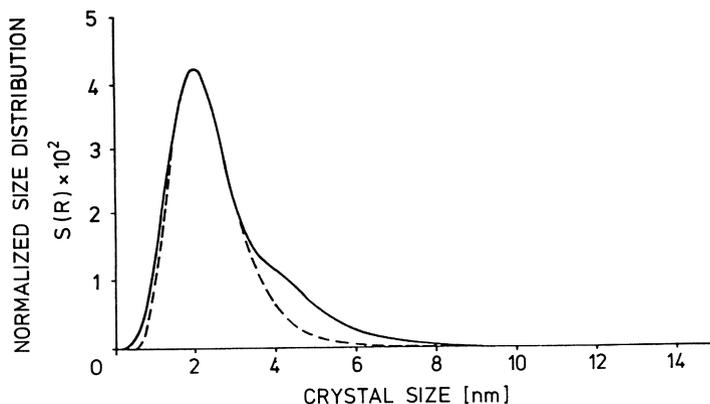


FIG. 5 Normalized size distribution of nanocrystalline Pd obtained from the small angle scattering measurements. The broken line represents the log-normal distribution.

STRUCTURE

In the previous paragraph, the two characteristic features of a solid consisting of a large volume fraction of grain boundary cores were pointed out to be (i) a reduced atomic density in the boundary regions and (ii) a broad spectrum of interatomic spacings coupled with a large variety of the nearest neighbour configurations in comparison to the perfect crystal.

Both features seem to be born out by the experimental observations. High resolution microscopy (2), and X-ray diffraction on Au-bicrystals (5), (30) indicate a reduction of the atomic density in the core region between 15 and 40%. Similar numbers are suggested by recent theoretical studies on boundaries in bicrystals (78). Small angle scattering measurements on nanocrystalline Pd (29), (31), and TiO_2 (32) indicated the average density in the boundary cores (width between 0.5 and 1 nm) to be reduced by about 20 to 40% relativ to the crystal density. Information about the atomic arrangement in the boundary cores of nanocrystalline materials was obtained by static and dynamic studies. EXAFS measurements (33) indicate a reduction of the number of nearest, next nearest etc. neighbours averaged over

all atoms of a nanocrystalline material relative to a single crystal (Figs. 6a and 6b).

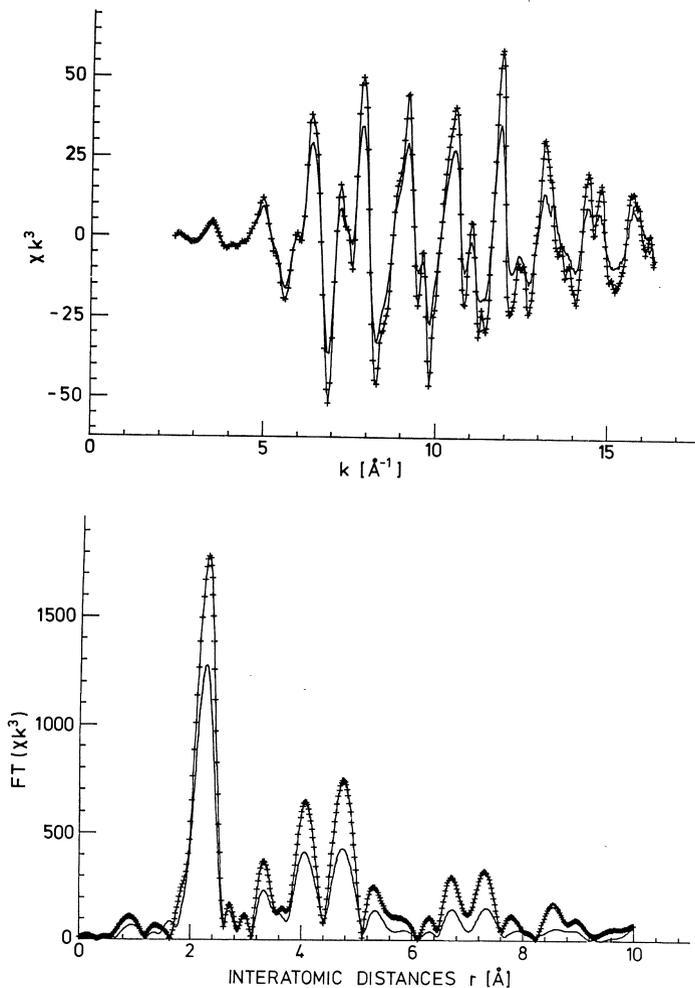


FIG. 6a,b The weighted EXAFS oscillations χk^3 (Fig. 6a) and the corresponding Fourier transform FT (χk^3), (Fig. 6b, phase shift is not included) of a nanocrystalline Cu sample (—) (crystal diameter: 10 nm) in comparison to polycrystalline Cu (+++). In the nanocrystalline sample the amplitude of the EXAFS oscillations and the FT (χk^3) are reduced relative to in the polycrystalline Cu (33).

This result may be understood, if the structure in the boundary cores differ from the structure in the lattice. In fact, the experimentally observed reduction of the EXAFS amplitudes and the corresponding Fourier Transform (Figs 6a, b) agrees with the idea (Fig 3) of a broad distribution of different nearest neighbour configurations in the boundary cores. A similar conclusion is suggested by Mössbauer spectroscopy measurements on nanocrystalline FeF_2 (34). The quadrupole splitting distribution of nanocrystalline FeF_2 is broadened (Fig. 7) relative to the one of an FeF_2 single crystal indicating a variety of atomic configurations with non-lattice symmetry to exist in the boundary cores.

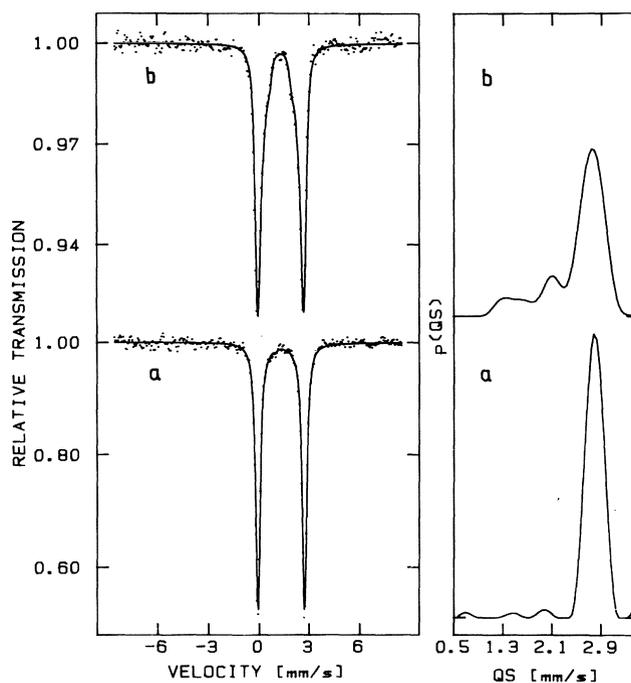


FIG. 7 The Mössbauer spectra and quadrupole splitting (Q.S.) distributions for coarse grained (a) FeF_2 powder and (b) nanocrystalline FeF_2 (77).

X-ray diffraction studies (35) on nanocrystalline Fe have been interpreted in terms of a boundary core structure in which the atoms are displaced from the ideal lattice sites of both crystals (Fig. 8).