MEASUREMENTS OF THE ELASTIC CONSTANTS, THE SPECIFIC HEAT AND THE ENTROPY OF
GRAIN BOUNDARIES BY MEANS OF ULTRA-FINE GRAINED MATERIALS

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Abstract. Measurements of the elastic constants, the specific heat and the entropy of grain boundaries have been performed by utilizing ultra-fine grained materials (Pd, 6nm grain size; Mg, 12 nm grain size; CaF_2 , 7 nm grain size) about 30 to 50 vol% of which consist of grain boundaries. The results obtained suggest that

(1) The interatomic potentials in grain boundaries in metals differ from the lattice potentials. Hence, the application of lattice potentials for computer simulation of boundary structures in metals may be of limited physical relevance.

(2) Boundary entropy effects are significant for the interfacial structure above half the absolute melting temperature.

(3) Metastable boundary structures with enhanced boundary entropies exist. The entropy enhancement may be several times the entropy of an equilibrated interface in the same material.

INTRODUCTION

If the crystal size of a polycrystal is reduced to a few (1 to 10) nanometers, the volume of the intercrystalline interfaces becomes comparable to the volume of the residual crystals. Such materials - called nanocrystalline materials - exhibit two features which distinguish them from all solid materials presently available and also indicate their potential for future technological applications. (i) The interfacial component exhibits a "gas-like" atomic arrangement (1) - (3). Hence, nanocrystalline materials differ structurally from all glassy ("liquid-like") and crystalline substances. (ii) The high volume fraction of interfaces permits the alloying of chemical components, e.g. metals and ionic crystals, that are immiscible in all glassy or crystalline materials (3). As a consequence, nanocrystalline substances exhibit properties which differ from those of conventional materials (2).

As this conference is primarily concerned with the structure and properties of internal interfaces, we shall focus attention on the question: what can one learn about the atomic structure of grain boundaries from the properties of nanocrystalline materials? Due to the large volume fraction of interfaces in nanocrystalline solids, their properties, e.g. their specific heat, results from the specific heat of the crystals as well as of the grain boundaries. If the contribution from the crystals is known, the boundary properties may be deduced and compared with the present interfacial models.

PREPARATION OF NANOCRYSTALLINE MATERIALS

Fig. 1: Schematic drawing of the arrangement used to generate nanocrystalline materials. Cf = cold finger, E = evaporator, C = compaction device.

Fig. 1 shows the experimental arrangement used to prepare nanocrystalline materials by a modified standard inert-gas condensation technique (e.g. ref 2). In the first part of the preparation process, the material (e.g. Fe) is evaporated from an electrically heated boat or crucible into an inert gas atmosphere (e.g. He) with a pressure of about 1 kPa. Due to interatomic collisions with the He, the evaporated Fe-atoms lose their kinetic energy and condense on a vertical cold finger (Cf) held at 77 K in the form of a loose powder ("Fe-black") the crystal size of which is a few, e.g. 5 nm. After restoring high vacuum ($< 5 \cdot 10^{-6}$ Pa) the powder is stripped off from the cold finger, and funneled into a piston and anvil device where it is compacted by applying a pressure of up to 5 GPa into nanocrystalline Fe, i.e. a Fe-polycrystal with a crystal size of 5 nm. The advantages of this method are as follows. (i) The crystal size can be manipulated by varying the He-pressure and the evaporation rate. (ii) The impurity content of the nanocrystalline material is 1 % or less because the system can be operated in a self-cleaning mode. The first Fe-atoms evaporated are used to getter the residual impurities from the He in the form of iron oxide, iron nitride, etc. crystals. These crystals are removed from the system by means of a separate cold trap before the production of the nanocrystalline powder is started. The impurities adsorbed at the walls of the evaporator were removed in the usual way by baking the system before evaporating the Fe.

PROPERTY MEASUREMENTS

Elastic constants.

The elastic constants of nanocrystalline materials were measured by two independent methods. (i) Elastic bending of a thin, plate shaped specimen supported at both ends and loaded with a constant force in the middle. The amount of bending was measured inductively with an accuracy of $\pm 2 \mu\text{m}$. The accuracy of the elastic modulus deduced from these measurements was $\pm 4 \%$. (ii) Measurements of the propagation velocity of a longitudinal or transversal sound wave (frequency 10 and

50 MHz) through nanocrystalline specimens. From the measured sound velocity (accuracy 2 %), the shear and the Young's moduli were computed by means of the standard equations assuming that the material is free of porosity. In fact, if a portion of the lower density of nanocrystalline materials would originate from macroscopic porosity, the elastic constants computed from the measured velocities of sound could be up to 5 % larger than the values listed in Table I. (iii) In transparent specimens the sound velocity was determined by Brillouin scattering using laser light with $\lambda = 358$ nm and a 90° diffraction geometry.

Specific heat. The specific heat, c_p , as a function of temperature was measured in a differential scanning calorimeter (Perkin Elmer DSC-2C) equipped with a low-temperature stage. The accuracy of the calorimeter was tested by measuring c_p of polycrystalline Cu and Pd discs (99.99 % purity) having the same mass and dimensions as the nanocrystalline samples. The deviation between the measurements on conventional polycrystals and the data reported in the literature (4), (5) was less than 2 % in the entire temperature range studied (150 - 300 K). The data at $T \leq 25$ K were obtained from ref. (15).

RESULTS AND DISCUSSION

1. Elastic constants

All metallic nanocrystalline materials which were investigated exhibited nearly the same elastic constants as conventional polycrystals. The opposite seems true for ionic crystals which showed a reduction of more than 50 % (Table I).

TABLE I: Elastic Properties of Nanocrystalline and Conventional Materials *)

Material	Crystal size (nm)	Young's modulus E (1000 N/mm ²)	Shear modulus G (1000 N/mm ²)
Pd	8	88 (123)	32 (43)
Mg	12	39 (41)	15 (15)
CaF ₂		38 (111)	19 (42)

*) The numbers in brackets indicate the values for an isotropic conventional polycrystals.

Due to the free volume of a grain boundary, the average interatomic distance in the boundary region is increased relative to the perfect lattice. If the interatomic potential in grain boundaries is assumed to be the same as in the perfect lattice, the elastic constants of a nanocrystalline material are expected to be reduced in comparison to the crystalline state. In fact, computer simulations of the elastic response of a [100] tilt boundary in Cu

and Al, assuming the same interaction potential in the boundary and the lattice suggest a modulus reduction due to grain boundaries (6). The reduction of E and G observed in CaF_2 (Table I) seems consistent with this interpretation. However, in order to understand the high elastic moduli of nanocrystalline Mg and Pd one is led to assume that the interaction potentials between atoms in grain boundaries differ from the interaction potentials in the perfect lattice in the sense that the interatomic coupling forces between boundary atoms are more sensitive to elastic deformations than in the perfect lattice. In order to test this interpretation, the grain boundaries of nanocrystalline Mg and Pd were doped with oxygen and water, by adsorbing (at 20°C) O_2 and H_2O at the free surfaces of the small Pd crystals prior to the compaction process. The interior of the crystals remained unchanged because both dopants cannot penetrate into the lattice at ambient temperature. If the elastic constants of the nanocrystalline substances depend on the interatomic forces in the boundaries, the incorporation of O_2 and H_2O should affect the elastic constants. Indeed, the doping reduced E and G to 31000 and 12000 N/mm². This interpretation agrees with the experimentally observed elastic moduli of composition modulated thin films when the wave length of the modulation approaches atomic dimensions. In fact, the periodic variation of the interatomic potentials due to the periodic chemical modulation has been shown (7), (8) to result in enhanced elastic constants. Hence, if it is assumed that the grain boundary regions of a nanocrystalline material can be regarded as regions in which the interatomic potential is modified relative to the potential in the lattices of the adjacent crystals, a similar modulus enhancement may be anticipated. Indeed, different interatomic potentials in grain boundaries and in the perfect lattice of metals have been proposed on theoretical (9) and experimental (10) grounds. Theoretical and experimental observations have indicated that the screening of the positive charge deficit of a grain boundary by the conduction electrons may result in an interaction potential which differs from the lattice potential. As a consequence, the results of computer simulations about the atomic structure of grain boundaries using lattice potentials may have to be considered with care. Only those computational predictions which are insensitive to the potential used may be of physical relevance. The rigid body relaxation between both crystals forming a grain boundary may be an example of this type. In fact, rigid body relaxation has been discovered by using a Morse potential (11), (12). In the subsequent years, experimental observations (13) as well as numerous computations employing a variety of other potentials have confirmed existence of this effect.

2. Specific heat

Nanocrystalline Pd (as compacted)

The measured excess specific heat (14), (15) of the as-compacted nanocrystalline Pd (6nm grain size) (Fig. 4) may be used to compute the excess entropy (S_i) due to the grain boundaries

$$S_i = \int_0^T \frac{\Delta C_p}{T} dT$$

where Δc_p is the difference between the specific heat of nanocrystalline and polycrystalline Pd and T is the absolute temperature.

Fig. 2: Excess specific heat (Δc_p) of nanocrystalline Pd (6nm). Δc_p is the difference between nanocrystalline and polycrystalline Pd. Curve 1: Pd, 6nm as-compacted. Curve 2: Same specimen after annealing at 530 K (1 min). The average crystal size has increased to about 10 nm.

If the Δc_p vs T curve (curve 1) is approximated by a straight line with the slope $A = 0.77 \cdot 10^{-25} \text{ J/at K}^2$ (Fig. 2), one obtains $S_i = AT_0$.

At $T_0 = 300 \text{ K}$ (Fig. 2); $S_i = 2.3 \cdot 10^{-23} \text{ J/at K}$.

If the volume fraction of grain boundaries is assumed to be 50 % at a grain size of 6nm, and if the atoms in the centers of the crystallites contribute little to the excess entropy, one obtains for $T \cdot S_i$ (per grain boundary atom in Pd) at $T_0' = 878 \text{ K}$ (50 % of the melting temperature of Pd)

$$T_0' \cdot S_i' = 1.2 \cdot 10^{-19} \text{ J/at.}$$

This entropy contribution to the free energy of a boundary is comparable with the internal boundary energy, U_i , of Pd:

$$U_i \approx 2 \cdot 10^{-19} \text{ J/at}$$

Nanocrystalline Pd (annealed at $\geq 350 \text{ K}$)

Nanocrystalline Pd specimens were observed to exhibit a reduced specific heat after annealing treatment of a few minutes between 350 K and 550 K (Fig. 2). During such an annealing treatment the average grain size changed little (less than a factor of two relative to the initial size) whereas the density of the material increased, suggesting a structural relaxation of the boundaries similar to the one reported for glasses upon annealing below the glass transition temperature. For the "relaxed" boundary

structure, the measured c_p -T-curve yields a much lower entropy per boundary atom in comparison to the as-compacted specimens (curves 1 and 2 in Fig. 2). For example if $T_0' \cdot S$ is evaluated from curve 2 (extrapolated to 0 K and $T_0' = 878$ K) one finds $T_0' \cdot S_1 = 3 \cdot 10^{-20}$ J/at. If the measured c_p -curve of the "relaxed" boundary (curve 2 in Fig. 2) is extrapolated to the melting temperature of Pd, T_m , one obtains an entropic contribution ($T_m \cdot S$) to the free energy of a grain boundary in the order of $1,2 \cdot 10^{-19}$ J/at which is comparable to the internal energy of about $2 \cdot 10^{-19}$ J/at.

The measured excess specific heat due to the presence of grain boundaries in Pd (Fig. 2) may be compared with the computed (19) excess specific heat of interphase boundaries. The experimental and theoretical data differ in magnitude and in temperature dependence. Ewing and Chalmers (16) estimated the boundary entropy by adapting an Einstein model to a computed grain boundary structure. The boundary entropy was found to originate from the lower vibrational frequency of boundary atoms, the availability of multiple equilibrium sites, and the anharmonic character of atomic vibrations. For a 22.6° symmetrical [001] tilt boundary in Au, the entropy contribution $T_m \cdot S_1$ was calculated to be $0.4 \cdot 10^{-19}$ J/at which is in the same order of magnitude as the value found for annealed Pd. Computer calculations (6) of the boundary entropy yielded comparable data. The experimentally observed large grain boundary entropy seems to agree with an enhanced Debye-Waller factor (17) and an enhanced thermal expansion coefficient (18) of grain boundaries deduced from X-ray scattering data and dilatometric measurements, respectively.

The following conclusions emerge from the observations reported on the specific heat and the entropy of nanocrystalline Pd. (1) At temperatures above half the melting temperature, boundary entropy effects become comparable to the internal boundary energy. Hence any comparison between computed and measured grain boundary structures and properties seems unrealistic unless entropy effects are included. Yet, in most comparisons published so far, this was not the case. (2) Metastable boundary structures of enhanced entropy seem to exist. The large entropy differences observed for "relaxed" and "unrelaxed" boundaries (Fig. 2) suggest differences in atomic structure, atomic mobility etc. between both types of boundaries.

GENERAL REMARKS

The structure and properties of grain boundaries in nanocrystalline substances may differ from interfaces in bicrystals with macroscopic dimensions in the following ways. (i) The high volume fraction (~ 50 vol%) interfaces in nanocrystalline materials results in boundaries with little solute segregation as the total solute content of the specimens was less than 1 %. (ii) The crystals of a nanocrystalline material are small and are surrounded by boundaries of different atomic structures. Hence the rigid body relaxation is expected to be different from the rigid body relaxation of a bicrystal with macroscopic dimensions. (iii) All data obtained represent an average over typically 10^{16} boundaries of different orientation relationships and inclinations.

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N.W. Ashcroft: 1) Have you determined the distribution of sizes of your particles (whose average size you quote). The issue is, how much small scale disorder you might have compared with genuine grain boundaries. 2) Have you plotted the excess specific heat in the conventional way for a metal (i.e. C/T vs T^2). Is it anomalous? [Comment: linear terms in C_p are common in glasses, but only at low temperatures.]