PART I

Properties of Nanocrystalline Materials
Kinetic and Thermodynamic Properties of Nanocrystalline Materials

R.S. AVERBACK, H. HAHN, H.J. HÖFLER*, J.L. LOGAS AND T.C. SHEN
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign
Urbana, IL. 61801

Abstract

A new class of materials with ultra small grain size has recently been synthesized by combining the methods of inert gas condensation of metal vapors and in situ powder compaction. These "nanocrystalline" materials, with grain sizes of 5-10 nm, have can have over 30 % of their atoms lying in the highly disordered interfaces or grain boundaries. Because of their unique atomic structure, nanocrystalline materials often have properties far different from their bulk counterparts. In addition, kinetic processes can be rapidly accelerated due to the short diffusion distances between grains. In this review, we will report on the thermodynamic properties and reaction kinetics of nanocrystalline metals and on such kinetic properties as sintering and grain growth in nanocrystalline ceramics.

I. Introduction

The synthesis and properties of nanoscale materials are becoming a major focus of materials science research. This interest derives from the possibility of controlling the atomic order of a material, and concomitantly, its properties. Most nanoscale research has been concerned with compositionally modulated thin-film structures because of their interesting electronic, optical and magnetic properties [1]. Recently, a method for producing three dimensional nanoscale structures has been developed by Gleiter and coworkers [2]. These new materials are comprised of nanoscale particles, typically 1-15 nm in size, which are compacted under high pressure to near theoretical bulk densities. Because of the small particle size, as many as 50 at % of the atoms can lie on grain or interphase boundaries. The interfaces of these particles are unique, as during the compaction step, the grains are constrained by their many interfacial contacts from rotating to lower energy configurations, creating a short range atomic order unlike crystalline or amorphous structures. Nanocrystalline materials have, in fact, sometimes been considered two-phase materials composed of distinct interface and crystalline phases [3] as shown schematically in Fig. 1. In nanocrystalline ceramics, pores are an additional important element of

Fig. 1 Schematic of a nanocrystalline material distinguishing between the crystalline phase, the interfacial phase and the pores between the grains.
the structure. Various experiments including EXAFS [4], x-ray diffraction [3], Mössbauer spectroscopy [5], positron annihilation [6] and Raman scattering [7], have all confirmed this two phase structure, although as can be seen from other contributions to this symposium [8], the nature of the interfacial phase remains controversial. In addition to structure, physical properties of nanocrystalline materials, magnetic, thermal, and mechanical, have also been found to differ significantly from their bulk counterparts [9].

Aside from their fundamentally new structure and altered properties, nanocrystalline materials are of interest because of their small grain size. A recent trend in the synthesis of advanced ceramic materials, for example, has been the reduction of particle size of the starting powder. One important advantage of small particle size is the reduced temperatures required for sintering. The strong dependence of densification rate on initial particle size in a monodispersed powder is explicitly shown by the expression,

\[ \rho = A \gamma_s / d^3 kT \left( D_b \delta_b / d + D_v \right) \]  

where \( \rho \) is the material density, \( \gamma_s \) is the surface free energy and \( D_b \delta_b \) and \( D_v \) are the grain boundary and bulk diffusivities, respectively [10]. A second strong motivation for using ultra-fine particles to synthesize ceramics and other brittle materials is the potential for providing ductility, superplasticity, and possibly fracture toughness. Karch et al. have recently reported that nanocrystalline (n-) TiO\(_2\) (rutile) and n-CaF\(_2\) show ductile behavior during deformation at room temperature [11]. As shown in Fig.2, TiO\(_2\) undergoes a brittle to ductile transition at room temperature on decreasing the deformation rate. Karch et al. tentatively explained their results on the basis of diffusional creep using the relation,

\[ \varepsilon = (\sigma \Omega d^2 kT)[B_1 D_v + B_2 D_b \delta_b / d] \]  

where \( \varepsilon \) is the strain rate, \( \sigma \) is the tensile stress, \( \Omega \) is the atomic volume and \( B_1 \) and \( B_2 \) are constants. Although there is some question whether diffusional creep is the correct mechanism for explaining the Karch et al experiment (see sections IV.1 and IV.3), it is clear from eqs. (1) and (2) that small grain sizes can have important advantages in synthesizing brittle materials. Moreover, the Karch experiment demonstrates, regardless of the mechanism, that nanocrystalline ceramics can be formed at low temperatures, indeed a useful property for materials processing.

Fig.2 Indentation of TiO\(_2\) at 20°C (a) showing ductile behavior in n-TiO\(_2\) using a load of 2N and loading time of 10 s. (b) showing brittle behavior (cracking) load (2N) is applied over 1 s. (c) showing brittle behavior in conventional TiO\(_2\) using a load of 5N and loading time of 10 s (after Karch et al. [11]).

Although nanocrystalline materials promise to be an important new class of materials, their potential for applications depends on a variety of factors. For structural components, the
nanocrystalline materials must be able to be sintered to near theoretical bulk densities without excessive grain growth. Control of grain growth will also be important if their potential for superplastic behavior at elevated temperatures is to be realized. The thermodynamic and diffusion properties of nanocrystalline materials also need to be determined to evaluate their potential for producing metastable materials. It is clear that nanocrystalline materials provide an abundance of research opportunities. In this paper, the initial progress toward understanding some of the thermodynamic and kinetic properties of nanocrystalline materials will be reviewed.

II. PROCESSING METHODS

The procedure for producing nanocrystalline materials has relied on a two-step process [2]. First, a source material is vaporized in an inert atmosphere of ≈ 100 Pa, where it condenses as fine particles. The particles are carried by convective flow to a cold finger where they loosely adhere. The inert gas is then removed from the chamber and the powder is scraped into a compaction device and isostatically compacted in a powder press at high pressures, typically 1-5 GPa, and various temperatures. Although some ceramics can be synthesized by this method, TiO$_2$ [12] and ZrO$_2$ [13] have been formed by post-oxidation of the metallic powder before it is scraped from the cold finger.

Joule heating has mostly been used to vaporize the source materials, although thermal evaporation processes have inherent limitations, e.g., alloys concentrations are difficult to control owing to the different vapor pressures of the constituent elements. It has been demonstrated that sputtering can also be used for producing ultra-fine particles. Recently, we have found that magnetron sputtering, either RF or DC, can be successfully employed for producing nanocrystalline materials [13]. To date, we have fabricated in our laboratory such metallic nanocrystalline materials as Zr, Mo, Al, Cu$_{90}$Mn$_{10}$ and Al$_{90}$Ti$_{10}$ using DC magnetron sputtering, illustrating that refractory metals and alloys can be obtained by this method. We have also used reactive RF magnetron sputtering to produce TiO$_2$. It thus appears that many types of materials can be synthesized by nanocrystalline processing.

III. RESULTS ON NANOCRYSTALLINE METALS

III.1 Thermodynamics

It is not surprising that the chemical potential of atoms residing in the interphase region of nanocrystalline materials differs from that in crystalline phases considering the open boundary structure. As a consequence, phase diagrams of the interphase region can differ widely from polycrystalline material. Two reported examples are H in n-Pd [14] and Bi in n-Cu [15]. For the former, Mütschele and Kirchheim demonstrated, using electrolytic charging, that the solubility of H in n-Pd is enhanced by a factor of ≈ 100 compared to that in polycrystalline Pd. They also observed that the interfacial phase does not transform to the β-phase as the crystalline phase does [16]. A similar enhancement of solubility was observed for the Bi - n-Cu system. By diffusing Bi into n-Cu at $T = 100{\text{°C}}$, Höfler et al. showed that the solubility for Bi in the interfacial phase of n-Cu is ≈ 20 at %, an increase of $10^5$ over that in polycrystalline Cu. The high solubility of Bi in n-Cu is reasonable considering (a) the excess volume in the grain boundary phase and (b) the complete miscibility of liquid Cu-Bi alloys.

Gleiter and co-workers have investigated the entropy of n-Pd and n-Cu by heat capacity measurements. Shown in Fig. 3 is the excess heat capacity $\Delta C_p$ of n-Pd ($C_p$ of the nanocrystal less $C_p$ of the polycrystal) plotted as a function of temperature [17]. At room temperature, the excess entropy is approximately twice the entropy of melting. If we assume the enthalpy of the nanocrystal is less than that of a liquid, then the nanocrystal is stable relative to a perfect crystal at elevated temperatures. At $T = 350{\text{ K}}$, however, the grain boundary structure of n-Pd relaxes, reducing the excess entropy - see Fig. 3. Nevertheless, the extrapolated Gibbs free energy of relaxed n-Pd remains greater than polycrystalline Pd at the melting temperature. Although evidence for this surprising conclusion is tentative, Gleiter et al. have reported that n-Pd...
is stable against grain growth during rapid thermal annealing near the melting temperature of Pd [18].

Fig. 3 Excess heat capacity of n-Pd as a function of temperature; (a) "as prepared" sample; (b) relaxed by annealing to 80 °C [17].

III.2 Reaction Kinetics

Altered free energies, short inter-grain distances and high diffusion paths in nanocrystalline materials can give rise to accelerated reaction kinetics. Höfler et al. have studied reaction kinetics in n-Pd by depositing thin films of Bi and Si onto its surface and monitoring the rate of compound formation. Rutherford backscattering spectra in Fig.4 show the reaction in the n-Pd - Bi system. At 120 °C, the Bi layer was completely reacted after 24 hours to form the intermetallic compound Pd$_3$Bi (determined by electron diffraction), which has a melting temperature of ~950 °C. A comparison sample comprised of a Bi/Pd thin-film diffusion couple remained unreacted for temperatures below 200 °C. Inert W marker atoms deposited at the initial Bi - n-Pd interface, revealed that the reaction proceeded by rapid dissolution of n-Pd into the Bi and precipitation of Pd$_3$Bi in the Bi phase. Similar results were observed for n-Pd - Si [15].

Fig.4 Backscattering spectra showing the formation of Pd$_3$Bi during interdiffusion of Bi and n-Pd.
An interesting possibility for the formation of metastable phases and fine-grained intermetallic compounds is provided by nanocrystal processing using binary powders. An example is the production of the intermetallic compound, CuEr, from elemental Cu and Er nanocrystalline powders [19]. Good mixing of Cu and Er was obtained by collecting the two powders simultaneously on a rotating cold finger. Upon compaction at room temperature, the material transformed directly to the intermetallic phase with no evidence of residual Er or erbium oxides. This procedure may be useful for producing metallic glasses by the solid state amorphizing transformation [20] or ductile intermetallic compounds. In the latter case, strengthening could be achieved by subsequent heat treatments to promote grain growth.

IV. RESULTS ON NANOCRYSTALLINE CERAMICS

IV.1 Pressureless sintering of pure n-TiO$_2$

Nearly all data of the properties of nanocrystalline ceramics have been obtained on TiO$_2$; these will be discussed in some detail to provide a starting point for understanding these materials. The densification and grain growth kinetics of n-TiO$_2$ have been studied for different processing and sintering treatments [21]. A “standard” sample was prepared as described in section II and refs. 12 and 21; the compaction temperature and pressure were 150 °C and 1.4 GPa, respectively. X-ray diffraction of the “as prepared” standard sample showed that the stable rutile phase was the only phase present, with no evidence for unreacted Ti or other Ti-oxide phases. The composition of the sample was determined by Rutherford backscattering analysis to be oxygen deficient in the as prepared state, TiO$_{1.7}$, but after sintering at 300 °C, it became nearly stoichiometric, TiO$_{2}$, and at the same time, the color of the sample changed from black to white, the normal color of bulk rutile. Whether the as prepared samples were truly oxygen deficient rutile -TiO$_{1.7}$ does not exist in the equilibrium phase diagram- or if other oxide phases undetected by x-ray diffraction were present, is uncertain.

![Fig. 5 Density (open symbols) and grain size (closed symbols) of n-TiO$_2$ as a function of sintering temperature; included are data for pressure-assisted sintering and Y-doped n-TiO$_2$](image-url)
The density and grain size of the samples were determined as a function of temperature. The density was measured while the samples had open porosity by nitrogen adsorption and capillary condensation, and by gravimetry (using Archimede’s principle), otherwise. The grain size was monitored by x-ray diffraction (using the Scherrer formula), and transmission or scanning electron microscopy. Plotted in Fig. 5 are the grain sizes (from x-ray measurements) and densities of n-TiO₂ as a function of sintering temperature. Sintering times were 15 hours in all cases. The initial density, after compaction at 150 °C, is ~75% that of pure bulk rutile (4.25 g/cm³). This green body density is remarkably high considering that ideal packing of a monodispersed distribution of spheres yields a density of 78%. We tentatively attribute this high density to a combination of processing factors. During the initial oxidation of the Ti powder, burning is clearly visible, suggesting that particle temperatures rise well over 600 °C on the cold shroud. Particles in close proximity are therefore able to sinter and form dense agglomerates. The compacted powder is thus comprised of a bimodal distribution of dense agglomerates and small particles for which high densities are easier to achieve. We believe that densification during the pressing process occurs by a combination of grain boundary sliding and fracture of agglomerates as the green body density is found to be a strong function of compaction pressure. We note that the particle size determined from scanning electron microscopy (SEM) at this stage of sintering is larger than that determined by either x-rays or transmission electron microscopy (TEM) since the difference between particles and agglomerates can not be distinguished by SEM.

Fig. 5 illustrates that little densification occurs during pressureless sintering at temperatures below ~ 550 °C. Above 600°C, however, the density increases with temperature, reaching a value of 96-99% bulk density at 900 °C. These temperatures for sintering are far lower than those required for more standard titania powders. For example, it was observed that densification of TiO₂ with an initial particle size of 1.3 μm required temperatures in excess of 1100 °C for complete densification [22]. The reduced sintering temperature in n-TiO₂ is readily explained by eq.(1) above.

![Fig. 6 Scanning electron micrographs of fractured surfaces of n-TiO₂](image)

While densification begins at 600 °C, Fig. 5 illustrates that the grain size remains stable until the sintering temperature exceeds 800 °C. Rapid grain growth takes place at temperatures of ~ 1000 °C. Although various microstructural features can suppress grain growth,
we suspect pore drag is the stabilizing force below 800 °C. A qualitative picture of the pore structure can be obtained from SEM micrographs, as illustrated in Fig. 6 which shows fracture surfaces of n-TiO$_2$ after different sintering treatments. The as prepared sample (left side) has the typical appearance of a green body material in the initial stages of sintering: residual porosity, rounded particles and interparticle contacts.

A quantitative study of the pore size distribution has been performed using nitrogen gas condensation and BET (Brunauer, Emmett and Teller) measurements [21]. In Fig. 7 are shown the total porosity and surface area after different sintering treatments. The sharp decrease in surface area at 550 °C shows that microstructural changes take place at temperatures below that necessary for densification. The total porosity begins to decrease rapidly above ~600 °C becoming closed at 700 °C. The reduction of pore surface without loss of pore volume during sintering below 600 °C suggests that surface diffusion provides the necessary mass transport. Diffusion measurements described in section IV.3 support this conclusion. Although the porosity of n-TiO$_2$ is relatively low for a green body ceramic, 25 %, it has important implications for deformation mechanisms. We believe this porosity strongly influences the deformation study of Karch et al. cited above.

![Graph](image)

Fig. 7 Total porosity (open symbols) and surface area (closed symbols) determined by BET measurements as a function of sintering temperature; included are data for pressure-assisted sintering.

### IV.2 Effects of Pressure and Yttrium doping on Sintering

Important considerations in evaluating the utility of nanocrystalline ceramics are whether enhanced sintering and superplasticity can be achieved at temperatures below those where grain growth occurs. Fig. 5 illustrates that complete densification by pressureless sintering of pure n-TiO$_2$ can not be achieved without some grain growth. Moreover, the temperatures available for superplastic straining would be restricted to below 850 °C, although, to date, the constitutive relations for n-TiO$_2$ deformation have yet to be obtained. To increase the driving force for densification but not grain growth, n-TiO$_2$ was sintered by hot isostatic pressing using = 1 GPa at 450 and 550 °C. Fig. 5 shows that densification is significantly enhanced by this procedure, attaining a density of >95% at 550 °C, while grain growth is suppressed. Doping treatments can also influence grain growth as seen in Fig. 5 for additions of 1.8 and 7.7 at. % Y to TiO$_2$. In this case, grain growth is notably suppressed while densification is somewhat enhanced.
IV.3 Diffusion in n-TiO$_2$

Values of grain boundary diffusion coefficients are important for understanding kinetic processes in nanocrystalline materials. For example, densification and diffusional creep rates, as indicated by eqs. 1 and 2, are directly proportional to grain boundary diffusion coefficients. Values for grain boundary diffusion are not available in most ceramics, nor is it likely that such values would apply to nanocrystalline materials, in any case, due to their unique grain boundary structures. Preliminary measurements of diffusion have now been performed on n-TiO$_2$ using Hf tracer impurity atoms [23]. The samples were prepared for these experiments by depositing a thin layer of Hf, ≈ 2.5 nm, onto the n-TiO$_2$ surface. Diffusion profiles were obtained using Rutherford backscattering analysis as shown in Fig. 8a,b. The diffusion behavior is strongly dependent on the sintering pretreatment. Shown in Fig. 8(a) are backscattering spectra from samples which were preannealed at 100 °C in vacuum prior to deposition of the marker and diffusion annealing. The reduction in the Hf yield at the highest energies in the spectra, which corresponds to Hf at the specimen surface, shows Hf diffusion into the bulk. Even at 150 °C, Hf diffuses somewhat into the n-TiO$_2$. After annealing at 300 °C, the Hf disappears from the surface, diffusing into the nanocrystalline ceramic at very low concentrations. Since the BET results show open (interconnected) porosity in similarly prepared samples, surface diffusion is the most likely diffusion mechanism at this stage. In order to prevent fast surface diffusion and measure grain boundary and volume diffusion, a sample was sintered prior to the Hf deposition under 1 GPa at 550 °C (see section IV.2), resulting in a density of 98 % and no interconnected pores (Fig. 5). The corresponding backscattering spectra are shown in Fig. 8b. As expected, no diffusion is observed at temperatures below 500°C. At 650 °C, the diffusion coefficient is $\approx 4 \times 10^{-13}$ cm$^2$/s, which is approximately the same as that of the self diffusion coefficient of Ti in single crystalline rutile. Since Ti is fast diffusing in TiC$\alpha$, these preliminary results that bulk diffusion is at least as rapid as grain boundary diffusion, may be reasonable, although here we have measured Hf tracer impurity diffusion and not Ti self diffusion.

Fig. 8 Hf-diffusion profiles in n-TiO$_2$ measured by Rutherford backscattering after different sinter treatments prior to Hf deposition; left side: (a) sintered without pressure at 100 °C; right side: (b) sintered at 1 GPa at 550 °C.