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Grain Boundary in Some Nano-Materials

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Abstract: The results from present high resolution electron microscopy studies revealed that the structures of the grain boundaries in NiO nano-material are amorphous and, on the other hand, the structures of grain boundaries in the ZrO_2 nano-material are crystalline. This is quite similar to the conventional zirconia ceramics. For the hydroxyapatite (OHAP) nano-material in human enamel (HE), the structures of grain boundaries are crystalline in some areas and amorphous in other areas. The man-made OHAP, however, has only crystalline GB area. The present investigation also revealed that in some nano-materials, such as SnO_2, the grain boundaries could be crystalline or amorphous, depending on heat treatment and other processing conditions. This is quite different from the conventional tin dioxide which has no amorphous grain boundary under any circumstances. Furthermore, in all cases, the lattices along grain boundaries in the nano-materials are distorted in appearance.

INTRODUCTION

The materials, which have nano-level grain size, have been investigated for years since they have unusual mechanical, thermal, optical and electrical properties.[1–3]

Obviously, the much higher grain boundary (GB) ratio (see Table 1) and the larger number of atoms at the grain boundaries in comparison with conventional materials, which have the micro level grain size, should be in some way responsible for these properties. The structure of the grain boundary should also have a significant effect on the performance.

The GB structures of nano-materials have been studied for years, with a number of experimental methods and techniques; and quite different conclusions were reached.

According to the results from X-ray diffraction, Mossbauer spectroscopy and extended X-ray absorption fine structure (EXAFS), the GB structure in the nano-materials was proposed as 'gas like', a kind of 'random structure' with the absence of long and short range orders.[4–6]

However, by using high resolution electron microscopy combined with Raman spectroscopy and small angle neutron scattering experiments, the grain boundaries, both in TiO_2 and Pd nano-materials, show no such 'random structure'. On the contrary, grain boundaries were similar to those of coarse grained conventional materials.[7–8]

Furthermore, recent work indicated that the grain boundaries in Pd and $(Fe_{0.99}Mo_{0.01})_{78}Si_9B_{13}$ nano-materials consist of both ordered and disordered regions.[9]

In the present paper, it will be shown that the grain boundaries in NiO nano-material are amorphous, in ZrO_2 nano-material are crystalline and in OHAP nano-material are both crystalline and amorphous depending on the biochemical condition; on the other hand, in some nano-materials, such as SnO_2 nano-material, the grain boundaries are amorphous, but could also become crystalline under proper heat processing conditions.

EXPERIMENTAL

In order to compare the GB structural features of different kinds of nano-materials, a variety of nano-materials, NiO, SnO_2, ZrO_2 and hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ were chosen to be characterized by high resolution electron microscopy. Since the processing and techniques of making the samples might seriously effect the GB structure,

different sample-making methods and processing conditions were adopted for study and comparison of the obtained GB structures.

Among them, the NiO nano-material, in a thin film form with thickness of 20–30 nm, was made by using a magnetic sputtering method; and different substrates were used and compared.

The ZrO_2 nano-material was prepared by low temperature sintering from nano-sized zirconia powder.

The SnO_2 nano-material was firstly prepared by 2 GPa pressure from superfine powder with a grain size of about 3–5 nm and then underwent heat treatment at different temperatures.

The HE nano-material in this study was chosen from adult human enamel. The samples were cut, polished and ion milled before being ready for HREM observation as reported in detail in our previous work.[10–12]

The specimens prepared from the above materials were characterized by X-ray diffraction and electron microscopy, especially the high resolution microscopy JEOL 4000EX and the analytical model JEOL 2000FX.

RESULTS AND DISCUSSIONS

In comparison to conventional polycrystalline materials, which have typical grain sizes on the scale of several micrometers, the ratio of grain boundary to bulk area in the nano-materials with their grain sizes ranging from several to dozens of nanometers should increase appreciably. In order to analyze the effect of grain boundaries on performance in more detail, a comparison of the GB vol % (volume percentage) between nano- and conventional materials has been made (Table 1).

From Table 1 it can be seen that the GB vol % of nano-material with a grain size of about 20 nm is 100 times higher than that of conventional material. And if the grain size in the nano-material decreases to 3–5 nm, the GB vol% will accordingly increase to 50%. Therefore, it would not be surprising if nano-materials possess some special properties, especially mechanical properties.

Table 1. GB vol% comparison between nano- and conventional materials

Materials	Conventional	Nano-			
Grain size (nm)	2000	20	10	4	2
GB thickness (nm)	0·6	0·6	0·6	0·6	0·6
Grains in $2\times2\times2\ \mu m$	1	10^6	$0{\cdot}8\times10^7$	$1{\cdot}3\times10^8$	10^9
GB vol%	0·09	9·0	18·0	42·6	80·5

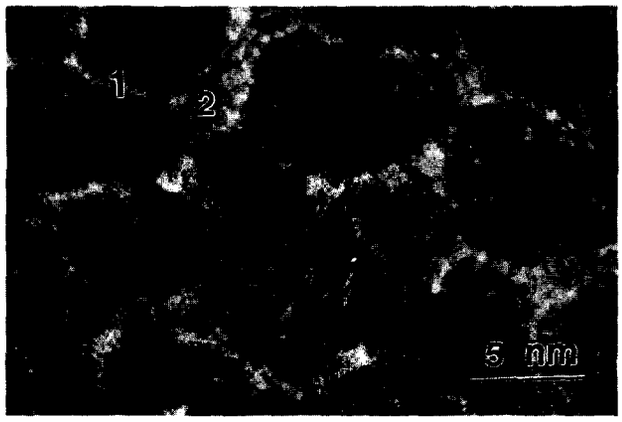

Fig. 1. HREM image of NiO nano-material, showing grains, grain boundaries and their microstructural features.

NiO nano-material

The NiO film made by magnetic sputtering with a grain size of about 3–8 nm has very valuable optical properties. The microstructure feature of these films is shown in Fig. 1. This is a high resolution electron micrograph, the electron beam being perpendicular to the surface of the substrate. These micrographs were taken at those areas of the specimen, in which the specimen thickness is of the order of the grain size, as overlapping or misoriented grains would make the electron micrograph difficult to interpret. There is no fundamental contrast change during focusing operation and specimen tilting. The grain boundary areas are always bright in contrast, and no lattice fringe contrast has been observed, showing an amorphous appearance. The grain boundary has a typical thickness of about 0·5–1·0 nm as shown at '1' in the figure, but in some triple points among grains, the amorphous areas are much wider than those between two adjacent grains as shown at '2' in the figure. On the whole, almost every grain seems to be surrounded by an amorphous layer. There are not many defects, such as microtwin, dislocation and stacking fault within the grains observed; however, lattice distortion and lattice bending along the grain surface were easier to observe in most areas.

Zirconia nano-material

The ZrO_2 nano-material, with grain size of several dozen nanometers, was prepared by about 1200°C sintering from super fine zirconia powder. The grain boundary and other microstructural features of this material are shown in detail in Fig. 2.

Figure 2 is a high resolution electron micrograph taken at 200 keV by using a JEOL 200 CX electron microscope. The observed areas in the specimen were ion-milled down to the thickness of about 10–20 nm.

Fig. 2. High resolution electron micrograph of ZrO_2 nano-material showing the grain boundary and other micro-structural features.

There was no obvious contour change in the grain boundaries through focus operation and specimen tilting. It can be observed that every grain has very clear fringe contrast and there is nothing else in the grain boundary except the lattice from adjacent grains. This shows that there is an abrupt lattice fringe stop among grains, indicating no random structure at the grain boundary.

Some GBs from two adjacent grains as shown at '1' in Fig. 2 have a very sharp abrupt fringe stop, indicating that not only is there no random structure but also no lattice distortion in the GB as in coarse-grained material.

However, a triple point as shown at '2' in Fig. 2 shows lattice distortion and lattice relaxation existed along the GB, and the lattice alters the periodic image structure.

OHAP nano-material

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, in human enamel and bone is a kind of natural nano-material made by the human body with a grain size of a few dozen nanometers in the enamel and several nanometers in bone. The typical microstructure features are shown in Fig. 3.

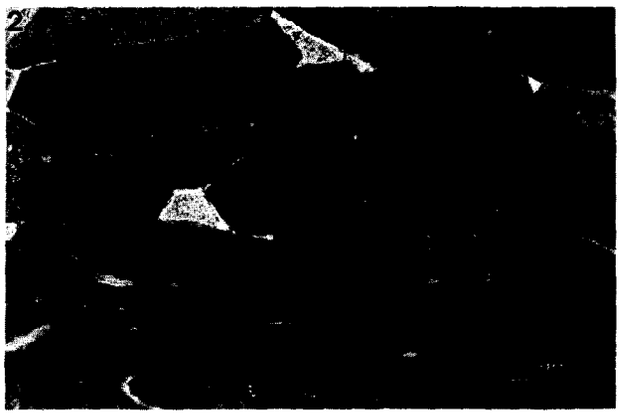

Fig. 3. HREM image of OHAP, showing GB and other microstructural features.

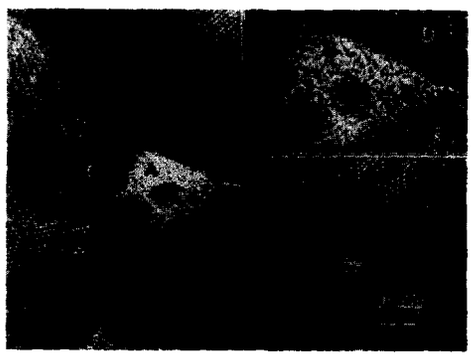

Fig. 4. HREM image of OHAP, showing amorphous area in the GB.

Figure 3 is an HREM image of OHAP in the enamel taken at 001 direction for all grains, which have the same direction along the *c*-axis but different directions along *a*- and *b*-axes. The grain boundaries in this material have two kinds of structure, which are completely different in nature.

One kind of GB is shown at '3' in Fig. 3. This is a GB from two adjacent grains indicating nothing else except a sharp lattice fringe from these grains.

Another kind of GB structure is shown at '1' in Fig. 3. This is a triple or tetrapoint among the grains with an amorphous contrast. Since the imaged area of the specimen should have a thickness of about 10–20 nm, only one layer of grains is left to be observed. In this case the Ar ion beam during the ion milling may sometimes make a grain move from its original position leaving a void in the observed specimen, which gives the image contrast like that at area '2' in Fig. 3.

A higher magnification electron micrograph is shown in Fig. 4, revealing the GB structure in detail. In Fig. 4, even smaller grains appeared among the amorphous area A, which is surrounded by the grains B, C, D, E and F.

The OHAP nano-material was produced in a human body after a very long period of time, but at low temperature (37°C). The grains are generally small and are oriented along the *c*-axis, and as a material it possesses very good mechanical properties. We have enough evidence to indicate that some amorphous areas in OHAP are originated from the carriers in human enamel.[11–12]

SnO_2 nano-material

The tin dioxide fine powder was prepared according to the following chemical reaction:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl$$

The obtained powders with grain sizes of about 3–5 nm were first pressed at 2 GPa pressure to shape it as a bulk material and then annealed at 200°C, 300°C, 400°C and 500°C, respectively, for 72 h.

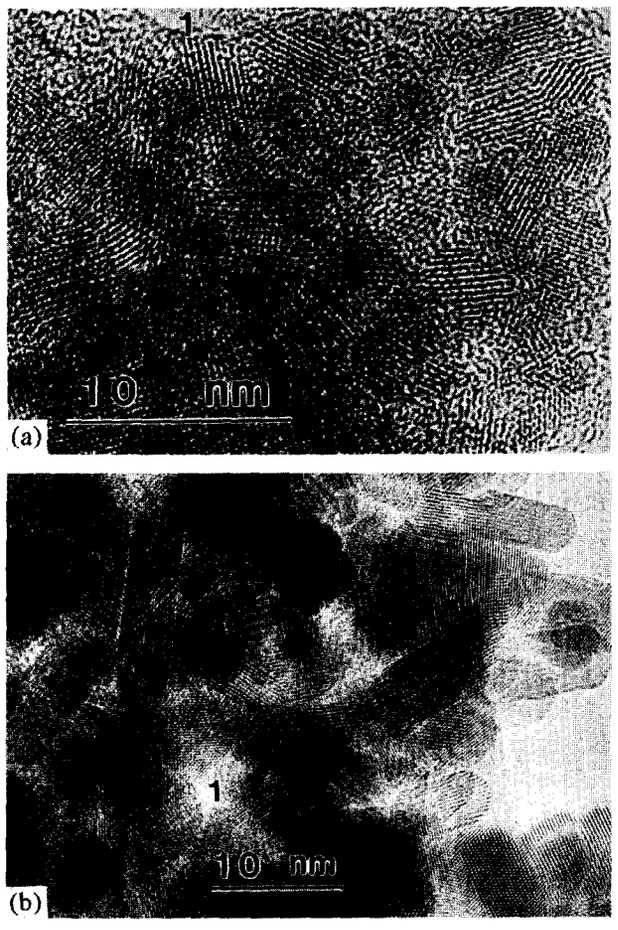

Fig. 5. (a) HREM image of tin dioxide nano-material treated at 200°C, showing the GB and other microstructural features. (b) HREM image of tin dioxide nano-material treated at 500°C [compare with Fig. 5(a)].

Both X-ray analysis and electron microscopy observations of these samples indicated that the grain boundaries in the material with low temperature annealing (200–300°C) are mostly amorphous and those boundaries annealed at higher temperature (400–500°C) are mostly crystalline.

Figure 5(a) is a high resolution electron microscopy micrograph showing the microstructure feature of tin dioxide nano-material which has undergone a heat treatment at 200°C for 72 h. It can be observed that the grains in the material are very fine at a level of 3–5 nm in size, and that the grain boundaries are not thin, and are sometimes as wide as 2 nm; each grain seems to be surrounded by an amorphous layer. The lattice within the grains is not very distinctive and serious lattice distortion and bending could often be observed. Since the material was not sintered, micropores usually of nanometer scale can be easily observed as shown at '1' in Fig. 5(a) and (b).

Figure 5(b) is a high resolution electron microscopy micrograph of the material which had been exposed to 500°C. It can be seen that the grain boundaries are thin and crystalline; the lattice within the grains is very distinctive; the grain size increases up to 5–10 nm and the grain shape also changes in comparison to those materials which were treated at lower temperatures.

CONCLUSIONS

In the present work, it is indicated that the structure of grain boundaries in nano-materials varies, depending on the material itself and the processing techniques used.

NiO nano-material in thin film form made by magnetic sputtering, has an amorphous grain boundary. The zirconia nano-material made by low temperature sintering has a crystalline grain boundary. This is very similar to conventional zirconia. The OHAP nano-material made by biochemical process has both amorphous and crystalline GB areas. The man-made OHAP, however, has only crystalline GB areas. The tin dioxide nano-material has either amorphous GB or crystalline GB depending on the heat treatment temperatures. The conventional tin dioxide, however, has only crystalline GB area.

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