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Nanocrystalline Borides and Related Compounds

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The data of hardness, Young's modulus, and electrical resistivity of TiN, TiN/TiB_2, and TiB_2 both for conventional and nanocrystalline materials in bulk and film forms are generalized. The hardness of TiN nanocrystalline bulk is 1.5 times higher than that of conventional materials. For monolayer and multilayer TiN films this value is about 2–2.5 and 3–3.5 higher than that for bulk TiN. The situation is similar for monolayer TiB_2 and TiB_2/TiN films. Their structure and properties are discussed in detail. © 1997 Academic Press

INTRODUCTION

In recent times nanocrystalline materials (NM), commonly characterized by a grain size less than 100 nm, have attracted attention because of the hope to realize unique physical, mechanical, and chemical properties (1–3). However, the main information on NM synthesis and properties concerns only some metals (Cu, Ni, Ag, Fe, etc.), intermetallics (TiAl, $NbAl_3$), and oxides (TiO_2, ZrO_2). Interesting compounds such as high-melting phases (borides, nitrides, carbides) were studied on a limited scale, although very promising results on nanocrystalline WC–Co hard alloys were obtained (4). Our attention is concentrated on TiB_2, TiN, and TiB_2/TiN NM because their wide application in the conventional polycrystalline state is well known. Besides that, the information on properties of these compounds in the conventional state is also comprehensive. Not only are particulate NM from ultrafine powders being investigated but also films from these compounds makes it possible studied. Such combination makes it possible to enlarge the spectrum of different structures and compositions and to compare properties of bulks and films.

One of the main problem in NM processing is consolidation with full densification without sacrificing their nanocrystalline structure. There are many methods of NM consolidation; some of them are shown in Table 1. Some intermediate methods must be added to this list such as crystallization from the amorphous state, plastic deformation, and dynamic recrystallization which can be used both for particulate materials and films and coatings. These methods have been discussed by us earlier (1). In many cases recrystallization results in a conventional structure with a grain size of about 1 μm and larger (1). In this connection only high-energy consolidation methods (e.g., high pressure sintering) and low-temperature film technology (e.g., magnetron sputtering) seem to be the most effective (5–8).

In this paper we focus attention on the comparison of properties of NM with conventional materials. We have used high pressure sintering ($T = 1200°–1400°C$; $P = 4–7$ GPa) and r.f./d.c. magnetron nonreactive sputtering for TiN bulk and TiB_2/TiN film preparation respectively. The features of synthesis and consolidation have been described elsewhere (1, 5–8).

Before proceeding to our analysis it is necessary to give some comments. For the comparison of NM with conventional materials we have selected three properties: hardness, electrical resistivity, and elastic modulus. This choice is connected with both known different structural sensitiveness of these properties and their practical importance. We also have given consideration to the characterization of our specimens with respect to composition, porosity, and grain size but this study is not finished yet.

RESULTS AND DISCUSSION

Table 2 shows some properties of TiN, TiB_2, and TiN/TiB_2 materials in different structure forms. As there is much information on this question for conventional materials (see, for example (9, 10)), we tried to use only the best results for well-characterized pore-free specimens. Unfortunately, data for the majority of TiB_2 and TiB_2/TiN nanostructured materials are absent. The results of (36, 37) are not included in Table 2 because of high porosity (13–16%). Structural information is presented in (8, 11–35). It is trivial for conventional materials and TiN NM. However, for TiB_2 and TiB_2/TiN films this information reveals AlB_2/NaCl-type phases or many phases or partly amorphous states (32, 34, 35). It is worth mentioning that a comparison also demands a detailed consideration of the effect of methods (for example, influence of load and substrate on hardness testing), and composition.

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TABLE 1
Main Preparation Methods of NM

Type of material	Preparation method
Particulate materials	Compaction and sintering; hot compaction (including HIP); hot forging; high pressure and high temperature technique; shock compaction; electro-discharge compaction
Films and coatings	CVD; PVD; electroplating; sol–gel technology

With regard to these many factors, a close inspection of Table 2 permits the following conclusions:

(1) TiN NM are the most extensively studied cases. The possibility of increasing the hardness value 1.5 times for bulk and 2–2.5 times for films is evident. This is the result of the nanocrystalline structure effect. In the case of nanostructured multilayer nitride films this benefit is still higher (about 3–3.5 times) (38, 39). Elastic properties are unchanged in the investigated grain size interval. This is also true for a recent study of metal NM (40). Low ρ values have been obtained for very perfect TiN films (15, 16, 20). The scatter in the ρ values of 40–600 μΩcm (see, for example, review [41]) reflects the influence of composition and grain size. A detailed investigation of size effect as applied to hardness and electrical resistivity of TiN NM seems to be necessary.

(2) The latter conclusion is also related to TiB_2 and TiB_2/TiN NM, especially as this information is very limited and results are available only for films. As in the case of TiN films the hardness value of TiB_2 films is about two times higher than that of conventional materials (the estimated H_v values for thin films, so called (7), are shown in parentheses). However, ρ for boride films is very high. It is reasonable that this is connected with the effect of admixtures, structural vacancies, and grain size on scattering of the carriers. At the same time it is difficult to divide the influence of these factors in itself.

(3) Special attention must be devoted to grain size determination. The analysis has shown that many methods such as XRD, TEM, and SEM are necessary for a representative discussion (41). Data in Table 2 seem to give only an estimate. Figure 1 shows the fracture surfaces of films

TABLE 2
Hardness (H_v), Young's Modulus (E), and electrical resistivity (ρ) of TiN and TiB_2 Materials

Specimen grain size (nm)	H_v (GPa)	E (GPa)	ρ (μΩcm)
(A) TiN materials			
Bulk	17.2 ($TiN_{1.0}$) (11)	618 ($TiN_{0.95}$) (12)	25($TiN_{0.99}$) (13)
	22.2 ($TiN_{0.77}$) (11)	480 ($TiN_{0.87}$) (12)	
	21.7 ($TiN_{0.96}$) (14)		
Single crystal	22.6 ((111) $TiN_{\sim 1}$) (15)		18($TiN_{\sim 1}$) (15)
Bulk (NM) 50–70	26.2($Ti(N_{0.96}C_{0.01}O_{0.03})_{\sim 0.9}$	490 (5,8)	
30–40	28.8($Ti(N_{0.92}C_{0.04}O_{0.04})_{\sim 0.87}$	490 (5,8)	
Film (NM) $\sim$ 20 (16)	35 (TiN_x) (16)	637 ($TiN_{\sim 1.0}$) (17)	20 (TiN_x) (16)
	43.6 (TiN_x) (18)	550 ($TiN_{0.97}$) (19)	26 ($TiN_{\sim 1.0}$) (20)
$\sim$ 20 (21)	45 (TiN_x) (21)	450 ($TiN_{\sim 0.8}$) (22)	
(B) TiB_2 materials			
Bulk	33.5 (14); 33.7 (25)	578 (23); 554 (26)	9 (24)
Single crystal	(0001) 27–27.5	(*a*) 185–193	6.6 (24)
	$(10\bar{1}0)$ 22.7–24	(*c*) 208–215 (24)	
Film (NM)	53 ($TiB_{\sim 2.8}$) (27)		500 (28)
	63.7 (29)		260 (30)
(C) TiN/TiB_2 materials			
Bulk		300–490 ($TiN_{0.9}$ + TiB_2) (33)	
Film (NM)	58 ($TiN_{\sim 1.4}B_{\sim 1.0}$) (27)	640 ($TiB_2N_{0.6}$) (34)	
	48 ($TiB_{1.4}N_{0.5}$)	750 (34)	
	52 ($TiB_{0.7}N_{0.5}$)	453 (34)	
$\sim$ 3	27 ($TiB_{0.6}N_{0.5}$)	276 (34)	
$\sim$ 6	40 ($TiB_{0.6}N_{0.5}$) (34)		
	35–45 ($Ti(B,N)_x$) (35)		
4–8	35.6 (49) ($(Ti(B_{0.73}N_{0.2}O_{0.07})_{1.56}$)	460	155 (32)
3–6	18.6 (49) ($(Ti(B_{0.34}N_{0.49}O_{0.17})_{1.49}$)	480	255 (32)

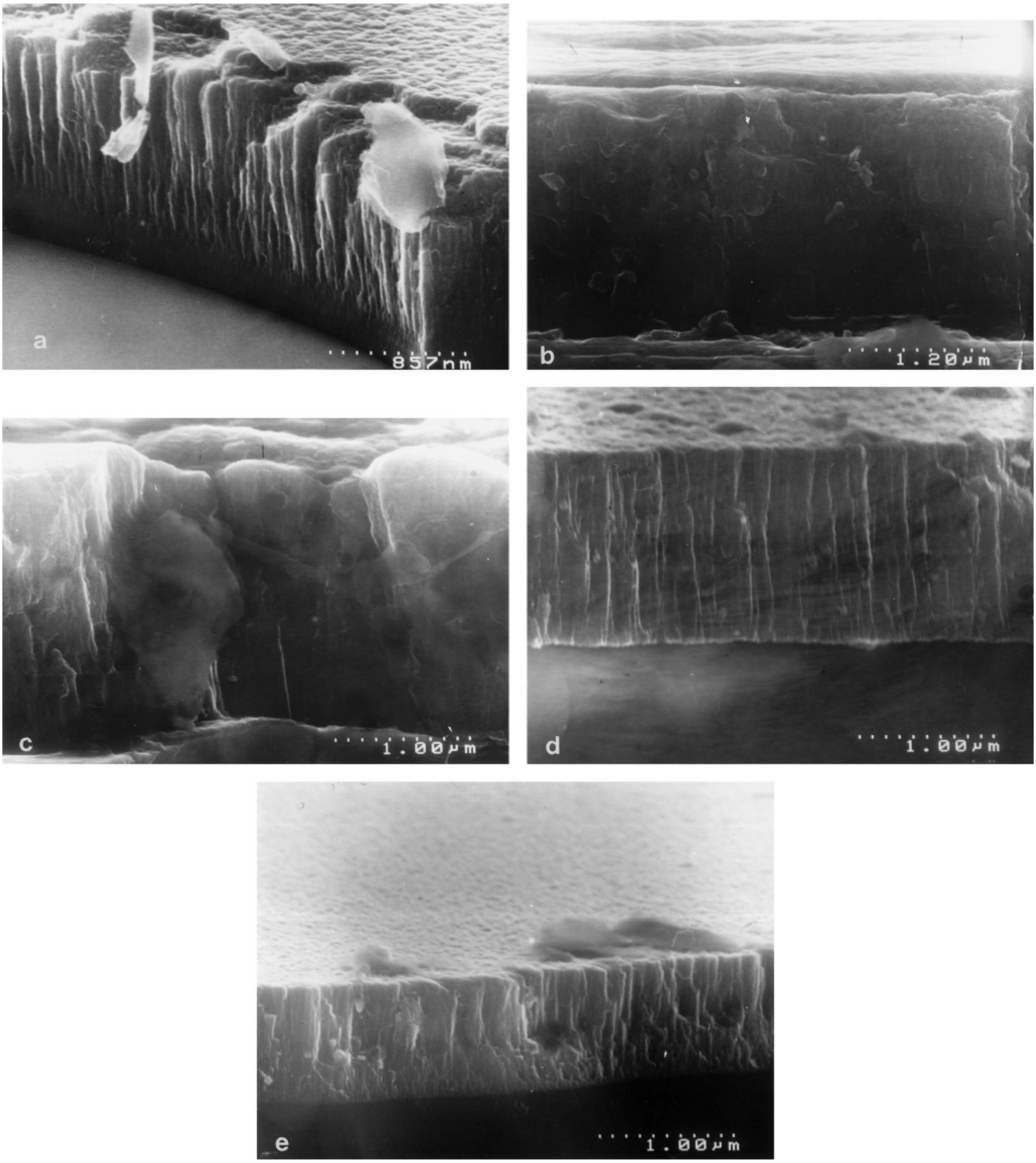

FIG. 1. High resolution SEM image of fractured cross-section of films obtained by r.f. magnetron nonreactive sputtering from various targets: (*a*) TiB_2; (*b*) $75TiB_2/25TiN$; (*c*) $50TiB_2/50TiN$; (*d*) $25TiB_2/75TiN$; (*e*) TiN.

prepared by r.f. magnetron nonreactive sputtering using TiB_2, TiB_2/TiN (75/25, 50/50, and 25/75), and TiN targets. Stone-like or cauliflower-like fracture surfaces were observed for films obtained from 75/25 and 50/50 targets. Other films have more columnar structure (column cross size is about 50-100 nm). At the same time XRD and TEM examination has revealed a very fine crystallite size ranging from 3 to 8 nm (32, 34). Figure 2 shows dark field image and SAED

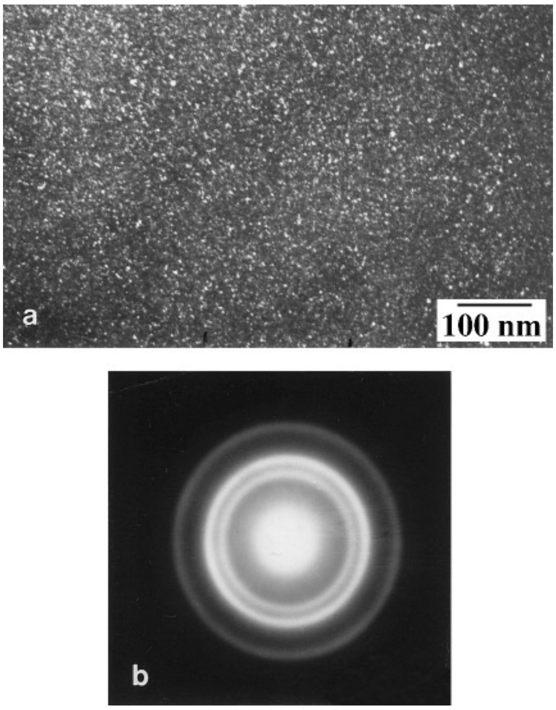

FIG. 2. Dark field TEM micrograph (line (101)) (a) and corresponding selected area electron diffraction pattern (b) of film deposited from $50TiB_2/50TiN$ target ($T_{substr} = 150°C$).

pattern of a film obtained from 50/50 targets (for comparison, see also SEM image in Fig. 1*c*). XRD and SAED examination revealed that this film had the cubic structure of NaCl type ($a \sim 0.42$ nm) and marked microstrains. Films obtained from TiB_2 and 75/25 targets were also characterized by a small grain size (4–8 nm) and had the hexagonal structure of AlB_2 type ($a = 0.3060$ nm; $c = 0.3201$ nm). The composition of these one-phase hexagonal ($(Ti(B,N,O,C)_{1.56}$) and cubic ($(Ti(B,N,O,C)_{1.49}$) films are listed in Table 2. Two-phase structures in the Ti–B–N films have also been described (34), and phase equilibrium in these films as a function of deposition conditions needs further study.

(4) It is well known that properties of nitrides and borides are changed in the range of homogeneity and defined by deviations from stoichiometry (9–12). As is evident from Table 2, synthesis of films is often accompanied by formation of nonstoichiometric films with high deviation from stoichiometry fixed by AES analysis (32). Such deviation is not common to conventional borides in bulk form (10). As is also seen from Table 2, our determinations of hardness and Young's modulus are comparable with the results of (34, 35). However, the explanation of these results is by no means easy because we have not information on influence of deviation of stoichiometry and phase content on films properties.

As is evident from the foregoing, only the first steps have been taken in the investigation of boride and nitride NM, and many problems, especially the size effect question and adequate structure characterization, remain unresolved and need further consideration and clarification.

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