

## Superhard Mo-Al-N films Composed of Grains with Different Crystallographic Orientations and/or Lattice Structures

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(Received 23 November 2002 ; accepted 23 December 2002)

### Abstract

This short communication reports on the experiment which demonstrates that superhard nanostructured films with hardness of about 40 GPa and greater can be composed not only of two or more nanocrystalline and/or amorphous *phases of different materials*, as it is in the case of nanocomposite coatings, but also that can be formed by a mixture of small (<10 nm) nanocrystalline *grains of the same material with different crystallographic orientations and/or lattice structures*. This finding opens new possibilities to develop advanced nanostructured materials with enhanced physical and functional properties.

*Keywords* : Mo-Al-N film, Hardness, Structure, Grain size, Mixture of grains

Recently, new superhard two-phase nanocomposite coatings with hardness greater than 40 GPa were successfully prepared using Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD) processes and their combinations<sup>1-5</sup>. First, it was believed that such superhard nanocomposites can be prepared only in the case when both phases of the nanocomposite are hard materials<sup>6</sup>. Very soon it was, however, recognized that this requirement is not necessary condition to produce superhard nanocomposites. A systematic investigation carried out on systems Zr-Cu-N<sup>7</sup>, Zr-Y-N<sup>8</sup>, Cr-Ni-N<sup>9</sup>, Zr-Ni-N<sup>10</sup>, Al-Cu-N<sup>11</sup> showed that superhard nanocomposites can be formed also in the case when only one phase is hard. This means that

there are two groups of the superhard coatings:

- 1) nc-MeN/hard phase (e.g. a-Si<sub>3</sub>N<sub>4</sub>, a-TiB<sub>2</sub>, etc.)
- 2) nc-MeN/soft phase (e.g. Cu, Y, Ni, Ag, etc.)

here, nc- and a- denote the nanocrystalline and amorphous phase, respectively, and Me=Ti, Zr, W, Cr, Mo, Al, etc., are elements forming hard nitrides.

The main feature of both groups of the superhard coatings is *the fact that these two-phase nanocomposite films are composed of two phases of different materials*. The hardness H of the films of both groups can be continuously varied from low values of approxi-

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mately 10 GPa to very high values achieving up to 50-70 GPa. These maximum hardnesses are more than twice higher than the hardness of the hardest component of the nanocomposite. This result, which is of great scientific and practical importance, however, opens two fundamental questions: (1) what is the origin of superhardness and (2) if the formation of two nanocrystalline phases of *different materials* is really only one way how to achieve the superhardness?

This letter is devoted to the second question. It reports on physical and mechanical properties of hard Mo-Al-N films, particularly on the structure-hardness relation in these films. The Mo-Al-N films were sputter deposited using an dc unbalanced magnetron with a composed target, i.e. a round Mo (99.5 % purity) plate of diameter 100 mm with a Al (99.99% purity) fixing ring of internal diameter 80 mm. They were

deposited onto polished and ultrasonically pre-cleaned CSN 15330 steel substrates (a disc 25 mm in diameter and 5-mm thick) under the following conditions: discharge current  $I_d$  ranging from 1 to 3 A, substrate bias  $u_s = -100$  V, substrate ion current density  $i_s$  ranging from 0.6 to 1.2 mA/cm<sup>2</sup>, two values of the substrate temperature  $T_s = 300$  and 500 (C, substrate-to-target distance  $d_{s-t} = 50$  mm, partial pressure of nitrogen  $p_{N_2}$  ranging from 0 to 0.5 Pa and total pressure  $p_T = p_{Ar} + p_{N_2} = 0.5$  Pa. Typical thickness of sputtered films was approximately 4  $\mu$ m.

Main results of this experiment follow from the correlation between the hardness and the structure of Mo-Al-N films, see Fig.1. In this figure the XRD patterns from the Mo-Al-N films of different chemical composition and sputtered at different values of  $p_{N_2}$  and  $T_s$  are given, see Table 1. The XRD patterns show that

- 1) The superhard Mo-Al-N films with ap-

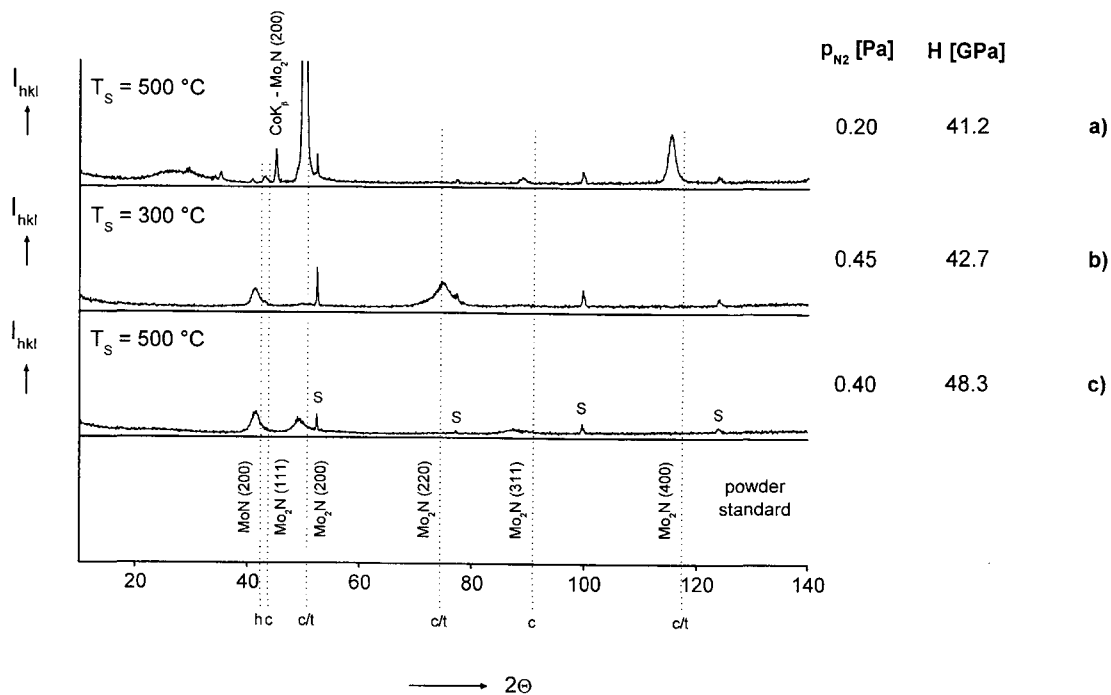


Fig. 1. XRD patterns from superhard Mo-Al-N films sputtered at  $I_d = 1$  A,  $u_s = -100$  V,  $i_s = 1.2$  mA/cm<sup>2</sup> and a)  $p_{N_2} = 0.2$  Pa,  $T_s = 500$  (C), b)  $p_{N_2} = 0.45$  Pa,  $T_s = 300$  (C) and c)  $p_{N_2} = 0.4$  Pa,  $T_s = 500$  (C).

Table 1. Deposition conditions, hardness, structure and chemical composition of three Mo-Al-N films whose XRD patterns are displayed in Fig.1.

film	$p_{N_2}$ [Pa]	$T_s$ [°C]	H [GPa]	$L_c$ [nm]	e	Mo [at.%]	Al [at.%]	N [at.%]	N/(Mo+Al)
A	0.20	500	41.2	30.5	0.004	60.1	1.8	37.7	0.61
B	0.45	300	42.7	3	0.026	47	1.9	50.2	1.02
C	0.40	500	48.3	5.4	0.025	49.6	1.8	48.3	0.94

proximately the same hardness H exhibit very different structures : 1) a well developed relatively narrow  $Mo_2N$  (200) and broad, low-intensity  $Mo_2N$ (311) reflections (the film with  $H = 41.2$  GPa, Fig.1a) and (2) (i) broad, low-intensity MoN (200) and  $Mo_2N$  (220) reflections (the film with  $H=42.7$  GPa, Fig.1b) and (ii) broad, low-intensity MoN(200),  $Mo_2N$ (200) and  $Mo_2N$  (311) reflections (the film with  $H=48.3$  GPa, Fig.1c). The same phenomenon was already observed for sputtered superhard Zr-Ni-N<sup>11)</sup> and Al-Si-Cu-N<sup>12)</sup> films.

2) The superhard Mo-Al-N films with hardness  $H \geq 40$  GPa are composed of two nc-grains of *different lattice structure of the same material* : (i) hexagonal MoN (200) and tetragonal and/or cubic  $Mo_2N$  (220) grains (Fig.1b) or (ii) hexagonal MoN (200) and tetragonal and/or cubic  $Mo_2N$  (200) grains (Fig.1c). Due to overlapping of the tetragonal  $Mo_2N$  and cubic ( $-Mo_2N$  reflections, it was not possible to determine if the Mo-Al-N film contains only one type of  $Mo_2N$  grains, tetragonal or cubic  $Mo_2N$ , or a mixture of both types of  $Mo_2N$  grains.

3) The orientation of grains in the Mo-Al-N film can also influence its hardness. The Mo-Al-N film composed of MoN (200) and  $Mo_2N$  (200) grains are harder than that composed of MoN (200) and  $Mo_2N$  (220) grains. At present, however, it is not clear what is really responsible for higher hardness : the orientation of grains

or the stoichiometry of the film? From Table 1 it is seen that the hardest Mo-Al-N film (the film C) is substoichiometric. This fact can also result in a higher hardness of the substoichiometric film compared to that of stoichiometric one.

The main result of this study is a finding that nanostructured materials can be superhard also in the case when they are composed of a mixture of nc-grains of different lattice structure. This means that hard and superhard nanostructured materials can be composed either of *grains of different materials* or can be formed by a *mixture of grains of the same material with different crystallographic orientations and/or different lattice structures*. This finding is of fundamental scientific and practical importance. It makes possible to explain the formation of the superhardness in single-phase materials, such as for instance W-Si sputtered films<sup>13)</sup>, which cannot be explained by an existence of two phases of different materials as it is in the case of nanocomposite materials.

Very interesting is also a correlation between the hardness, grain size and microstrain in Mo-Al-N films, see Fig. 2. Here, the dependences of the microhardness H and microstrain  $E_g$  in the film on an average grain size  $L_c$  are displayed. The values of  $E_g$  and  $L_c$  were evaluated from the broadening of the x-ray reflection line with

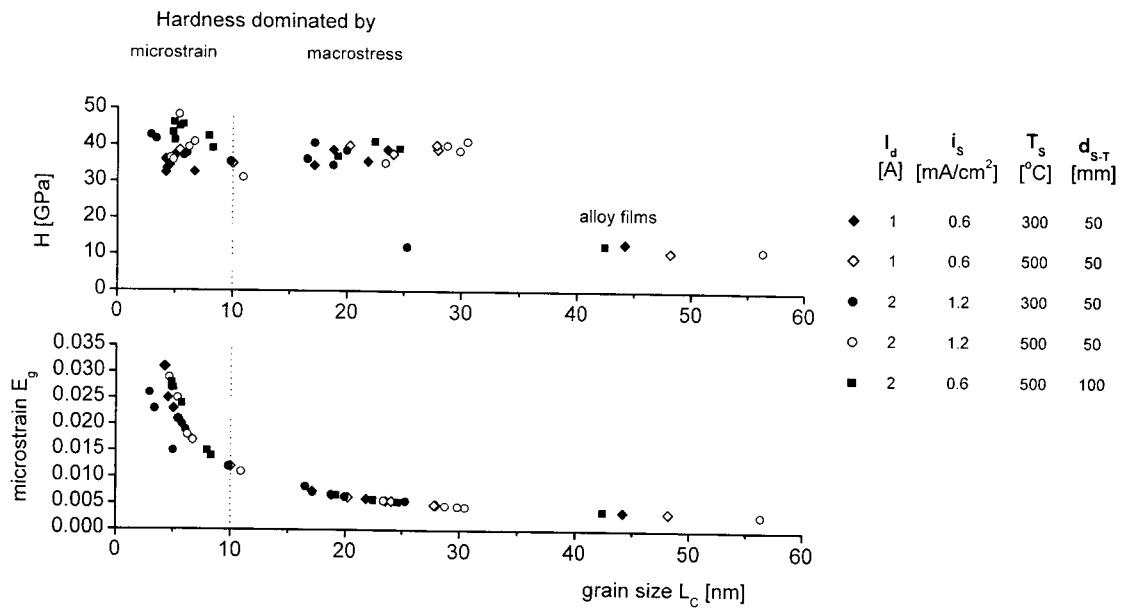


Fig. 2. The microhardness  $H$  and the microstrain  $E_g$  in sputtered Mo-Al-N films, sputtered at  $u_s = -100$  V,  $i_s = 0.6$  and  $1.2$  mA/cm<sup>2</sup>,  $I_d = 1$  and  $2$  A,  $T_s = 300$  and  $500$  (C),  $d_{s-T} = 50$  and  $100$  mm and  $p_T = p_{Ar} + p_{N_2} = 0.5$  Pa, as a function of the average grain size  $L_c$ . The microhardness  $H$  was measured using a computer controlled microhardness tester Fisherscope H 100 at a load  $L = 30$  mN of the Vicker's diamond indenter.

highest intensity, i.e. from a Full Width at Half Maximum (FWHM), using the Scherrer formula. From Fig. 2 it can be seen that

a) The hard Mo-Al-N films with the same microhardness  $H$  of about 35 GPa can be composed of grains of different size ranging from several nanometers to about 30 nm. The behavior of films with the same  $H$  composed of larger ( $> 10$  nm) and smaller ( $\leq 10$  nm) grains, however, strongly differs. It is connected with a strong change in (i) the film crystallinity from well developed relatively narrow reflections to broad, low-intensity reflections as shown in Fig. 1 and (ii) the microstrain  $E_g$  in the film.

b) The microstrain  $E_g$  increases with decreasing grain size  $L_c$  and a dramatic increase in  $E_g$  is observed for films composed of grains with  $L_c \leq 10$  nm. This strong change in  $E_g$  also correlates well with an occurrence of broad, low-intensity reflections in the XRD pattern.

c) Observed experimental data clearly demonstrate that there is no simple relation between the film hardness and the average size of grains. For more details, see for instance<sup>14)</sup>.

Recently, it was shown that a decrease in the grain size  $L_c$  below 10 nm results in dramatic changes in magnitude of the macrostress  $\sigma$  generated in the hard film during its growth. The superhard 4  $\mu$ m thick Al-Cu-N film with hardness of 47 GPa, composed of small ( $< 10$  nm) grains, exhibits a low compressive macrostress of about -0.2 GPa. On the contrary, the superhard 4  $\mu$ m thick Zr-Cu-N film with hardness of 54 GPa, composed of larger ( $\approx 30$  nm) grains, exhibit a high compressive macrostress of about -4 GPa<sup>15)</sup>. Therefore, the dependence  $H = f(L_c)$  in Fig. 2 is divided into two regions where the microhardness is dominated either by the macrostress  $\sigma$  in films composed of grains with  $L_c > 10$  nm or by the microstrain  $E_g$  in films composed of grains with  $L_c < 10$  nm. This finding is

also of fundamental importance and opens a new stage in investigation of hard nanostructured coatings. Therefore, a considerable attention is now concentrated particularly on (i) the grain size dependent phenomena and their correlations with properties of coatings and (ii) the control of energy delivered to the film during its growth. Also, the macrostress  $\sigma$ , generated in the Mo-Al-N film during its growth, was not so far measured and is now under study.

In summary, the investigation of the sputtered Mo-Al-N films showed that nanostructured materials can be superhard in the case when they are composed of a mixture of *nc-grains of the same material with different crystallographic orientations and/or different lattice structures*. This finding is of great scientific and technical importance because it (1) widens our knowledge on enhanced properties of nanostructured materials, (2) gives a new insight into the origin of superhardness and (3) makes it possible to explain the superhardness of single-phase materials when the concept of superhardness based on *different phases of different materials*, valid for nanocomposite films, cannot be used.

This work was supported in part by the Ministry of Education of the Czech Republic under Projects MSM # 235200002 and ME # 529.

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