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Some consequences of the partial crystallographic coherence between nanocrystalline domains in Ti–Al–N and Ti–Al–Si–N coatings

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Abstract

Formation of partially coherent nanocrystalline domains, development of intrinsic residual stresses and the relationship between the partial coherence of crystallites and the hardness of vacuum-arc-deposited Ti–Al–N and Ti–Al–Si–N nanocomposites were investigated for different chemical compositions of the nanocomposites using a combination of the electron probe microanalysis, X-ray diffraction, transmission electron microscopy with high resolution and hardness measurement. Partial coherence of nanocrystalline domains was found to be a very important microstructural feature, which is strongly related to the correlated orientation of neighbouring crystallites and to the atomic ordering at the crystallite boundaries. Appropriate mutual orientation of neighbouring crystallites and suitable atomic ordering at the crystallite boundaries facilitate the development of intrinsic residual stresses, which influence directly the hardness of the nanocomposites.

Keywords: Transmission electron microscopy; Nanostructures; X-ray diffraction; Hardness; Nitrides

1. Introduction

Nanocomposite coatings were proposed by Veprek et al. [1] about 10 years ago as novel promising super-hard materials. According to the Hall–Petch relationship [2,3], high density of grain boundaries was considered as the main reason for the extremely high hardness of this nanocomposites [4]. The optimum crystallite size was found to be approximately 3 nm [5–7], which is analogous to the optimum individual layer thickness observed in super-hard super-lattices [8,9]. The best performance of the nanocomposites shall be reached if the nanocrystallites are covered by one monolayer of an amorphous substance, e.g., a-Si_3N_4 or a-BN [7,10,11]. For machining applications, high toughness and good chemical stability at temperatures exceeding 1000 °C are required besides the high hardness [12–14]. Thermal stability of the super-hard nanocomposites was investigated comprehensively in the past [11,15–20]. These studies together with the considerations about the thermodynamics of the related systems yielded that the nanocomposites can be formed during a spinodal decomposition of immiscible or thermodynamically unstable substances [19,21–24].

The properties of nanocomposites can be explained only with the aid of detailed microstructure analysis. Therefore, the analysis of the crystallite size is an obligatory procedure in the studies of super-hard nanocomposites. It is usually performed through the analysis of the X-ray diffraction (XRD) line broadening. However, standard procedures based on the classical kinematical diffraction theory can yield quite unreliable results. This problem was discussed in [6], for instance. One source of this discrepancy is the decomposition process in immiscible or thermodynamically unstable or metastable systems [25], which, in nanocomposites, causes a partial coherence of neighbouring crystallites for X-ray diffraction [26]. This "crystallographic" coherence was described in [27] by a partial overlap of reciprocal lattice points for crystallites smaller than approximately 10 nm that causes a "narrowing" of XRD lines in nanocrystalline materials. Recently, our results on the partial coherence of crystallites [27] were supported by

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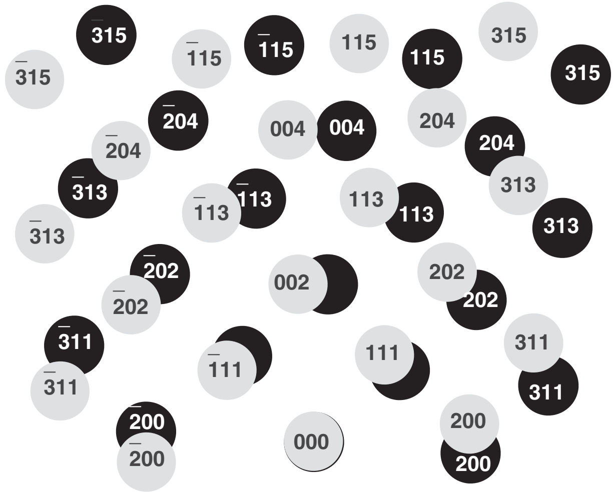

Fig. 1. Reciprocal lattice points of two mutually disoriented fcc crystallites (gray and black circles) projected into the *x*–*y* plane in the reciprocal space. The overlap of the reciprocal lattice points represents the degree of the partial coherence of the crystallites [27]. Numbers inside the circles are the diffraction indices.

Ribárik et al. [28] with results obtained on nanocrystalline powders.

In [27], we have shown that the “narrowing” of diffraction lines depends on the size of the diffraction vector, and thus on the diffraction angle, and on the mutual disorientation of crystallites having the same crystal structure. Most affected are diffraction lines measured at small diffraction angles. With increasing diffraction angle, the overlap of the reciprocal lattice points and thus the degree of the partial coherence of neighbouring crystallites decreases (Fig. 1). The diffraction lines broaden rapidly until the overlap of the reciprocal lattice points (the partial coherence of crystallites) disappears, which causes a rapid saturation of the diffraction line broadening. The saturated value of the line broadening corresponds to the true crystallite size [27]. The second parameter, which strongly influences the degree of the coherence of the neighbouring crystallites, is their mutual crystallographic orientation. The sharper the local texture, the smaller the disorientation of neighbouring crystallites and thus the stronger the effect of the partial coherence of crystallites on the XRD line broadening. In this contribution, we illustrate the relationship between the chemical composition of Ti–Al–N and Ti–Al–Si–N nanocomposites, their phase composition, crystallite size, global and local preferred orientation of crystallites, atomic ordering at the crystallite boundaries, partial coherence of neighbouring crystallites, amount of intrinsic residual stresses and hardness. The central issue of this contribution is discussion of the information contents of the partial coherence of crystallites.

2. Experimental details

Two series of samples were investigated in this study: one was based on the Ti–Al–N system and the second one on the Ti–Al–Si–N system. Each series consisted of seven samples with different [Ti]/([Ti]+[Al]) or [Ti]/([Ti]+[Al]+[Si]) ratio. The samples were prepared by arc evaporation in nitrogen atmosphere with the working pressure of 1.3 Pa using two laterally rotating arc-cathodes (π-80 from PLATIT) [29]. The base pressure was 5×10^{-3} Pa and the deposition temperature 450 °C. One cathode consisted of titanium; the other was made either from aluminium (for the Ti–Al–N system) or from aluminium with addition of 11 at.% Si (for the Ti–Al–Si–N system). The ion current on the Ti cathode was 80 A and on the Al (or Al–Si) cathode 120 A. The bias voltage was −75 V. Variable stoichiometry of the coatings was achieved by different distances and angles between the substrates and the respective cathode [30]. Another consequence of the variable distance and variable angle between the substrates and the respective cathode was a variation in the thickness of the thin films, see Table 1. Polished plates of cemented carbide were used as substrates as usual for coatings considered for high-temperature applications. In contrast to commercial coatings, where the substrates are typically rotated in the deposition process, our substrates were not rotated during the deposition in order to be able to correlate the local and the global preferred orientation of crystallites to each other that is necessary for explanation of the coherence phenomena in these coatings.

Chemical composition of the samples (Table 1) was determined using a combination of the electron probe microanalysis with wavelength-dispersive spectroscopy (EPMA/WDS) and the glow-discharge optical emission spectroscopy (GDOES). The chemical analysis using EPMA/WDS was performed in 40 points across each sample to inspect the lateral homogeneity of the chemical composition. The maximum deviation in the concentration of Ti, Al and Si calculated over these 40 points was below 2 at.% in all samples. GDOES was primarily used to measure the nitrogen contents in the coatings, which cannot be achieved using EPMA/WDS with a sufficient reliability because of the overlap of the spectral line Kα_1 of nitrogen with the L1-line of titanium.

Microstructure of the samples was investigated using a combination of X-ray diffraction (XRD) and transmission electron microscopy with high resolution (HRTEM). HRTEM was performed with a 200 kV analytical high-resolution transmission electron microscope JEM 2010 FEF (Jeol) equipped by ultra-high-resolution objective lens ($C_s = 0.5$ mm) and in-column energy filter to select only the elastic electrons

Table 1
Overall chemical composition, obtained from EPMA/WDS and GDOES, and thickness of the Ti–Al–N and Ti–Al–Si–N thin films under study

Chemical composition	Thickness (μm)	Chemical composition	Thickness (μm)
$Ti_{0.96}Al_{0.04}N$	2.7	$Ti_{0.96}Al_{0.04}N$	2.9
$Ti_{0.85}Al_{0.15}N$	4.7	$Ti_{0.85}Al_{0.14}Si_{0.01}N$	5.1
$Ti_{0.73}Al_{0.27}N$	5.8	$Ti_{0.72}Al_{0.26}Si_{0.03}N$	6.3
$Ti_{0.52}Al_{0.48}N$	6.1	$Ti_{0.53}Al_{0.42}Si_{0.05}N$	7.0
$Ti_{0.38}Al_{0.62}N$	5.5	$Ti_{0.40}Al_{0.53}Si_{0.08}N$	6.3
$Ti_{0.17}Al_{0.83}N$	5.2	$Ti_{0.20}Al_{0.71}Si_{0.09}N$	5.4
$Ti_{0.09}Al_{0.91}N$	3.7	$Ti_{0.07}Al_{0.82}Si_{0.11}N$	3.9