A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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NON-DESTRUCTIVE TESTING OF FGM-MADE STRUCTURAL ELEMENTS[1)]

NIENISZCZĄCE BADANIE ELEMENTÓW KONSTRUKCYJNYCH O STRUKTURZE GRADIENTOWEJ

Non-destructive testing of materials with laminar and gradient structure is one of priority research of temporary surface engineering. In that field crystallographic texture and residual stresses analysis in near-the-surface areas of structural elements become more and more useful. Recently introduced and verified experimentally the X-ray texture tomography (XTT) represents a non-invasive method of investigating the texture of the near-the-surface areas on X-ray penetration depth, usually up to *100 μm*. It allows to localize the texture changes occurring under the sample surface to a certain definite depth.

The study gives a review on application the XTT to analysis of a functionally graded material (FGM) as a non-conventional investigation its inhomogeneous structure. Principles of the XTT method for determination of texture depth-profile of the FGM-made layers are also presented. The nature of texture formation in the substrate/deposit composition is discussed.

Keyword: Functionally Graded Materials, Crystallographic Texture, Texture Inheritance, Near-surface Layer

Nieniszczące badania materiałów o strukturze warstwowej oraz gradientowej są jednym z priorytetowych kierunków rozwoju współczesnej inżynierii powierzchni, a analiza tekstury krystalograficznej i naprężeń własnych w obszarach przypowierzchniowych elementów konstrukcyjnych staje się coraz bardziej użyteczna w tym zakresie. Opracowana ostatnio rentgenowska tomografia teksturowa (RTT) reprezentuje nieniszczącą metodę badań tekstury obszarów przypowierzchniowych o grubości porównywalnej z głębokością penetracji promieni rentgenowskich, zwykle do *100 μm*. Pozwala ona zlokalizować zmiany tekstury zachodzące pod powierzchnią próbki do określonej głębokości. W pracy opisano zastosowanie RTT w analizie funkcjonalnych materiałów gradientowych cechujących się niejednorodną strukturą. Podano również zasady stosowania RTT w ocenie profilu głębokościowego tekstury materiałów gradientowych. Przedyskutowano wpływ podłoża na formowanie się tekstury warstwy w materiale warstwowym.

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[1)] invited lecture

1. Introduction

Functionally graded material (FGM) is a macroscopically inhomogeneous material that has a gradient in structure from one surface to another [1]. FGM is a two- or multi-component composite characterised by a compositional gradient from one component to the other. In contrast, traditional composites are homogeneous mixtures, and they therefore involve a compromise between the desirable properties of the component materials. Since significant proportions of an FGM contain the pure form of each component, the need for compromise is eliminated. The properties of the components can be fully utilised. For example, the toughness of a metal can be accompanied with the refractoriness of a ceramic, without any compromise in the toughness of the metal side or the refractoriness of the ceramic side.

A revival of the world's interest in gradient materials began the Japanese in 1984 during the space-plane project, in the form of a proposed thermal barrier material capable of withstanding a surface temperature of 2000 K and a temperature gradient of 1000 K in a cross section < 10 mm. FGMs are now being evaluated as a means of altering the mechanical, thermal, acoustic, electrical, or optical properties of composite materials. Altering these materials properties requires changing the chemical composition, microstructure, state, distribution pattern or other factors in the FGM layer interface between materials. These changes can take place over a relatively short distance, or over the entire length of the component being fabricated. In that sense, a nitrided steel, for instance, could be also regarded as a FGM.

Such compositions exemplify the structurally inhomogeneous and present the modern class of constructing materials. Among the FGMs' features determining its thick-profile (gradient) properties a crucial role plays a crystallographic texture. The texture is a statistical property of a material with crystalline structure manifested by the ordering of the spatial orientation of the particular crystallites (grains, sub-areas and particles). Hence, the texture is one of the most effective characteristics of microstructure of the FGMs.

The effective analysis of the texture can be carried out only in a way not disturbing a sophisticated arrangement of the layers and near-surface areas, formed most often deliberately in a technologically advanced process. Owing to the subtle system of residual stresses, liability of lattice modifications, meta-stability of phases, and so on, a non-destructive research tool for investigation of the inhomogeneous microstructure of the FGM is required. Such a tool becomes recently presented method termed as X-ray Texture Tomography (XTT) [2].

The XTT consists in a specific manner of the registration of the experimental data, so called constant-depth pole figures, and their mathematical transformation by introduced procedures. Registration of such figures can be realised only when a constant incidence angle of the beam on the sample is retained, which is possible by adopt the texture goniometer with the option of expansion of the scanning mode $\theta \leftrightarrow 2\theta$ to the $\omega \leftrightarrow 2\theta$ one. A specific combination of the sample tilting angles during measurement, creating a so called information valley, enables to keep the penetration depth at the constant level. An example of such information valley for *311-Al* reflection is shown in Fig. 1. As shown in the figure, it is possible to maintain the measurement conditions along a constant-level "path" of such a profile, i.e. the constant information depth related to a selected tomographic layer in the near-the surface area of investigated sample (see Fig. 1).

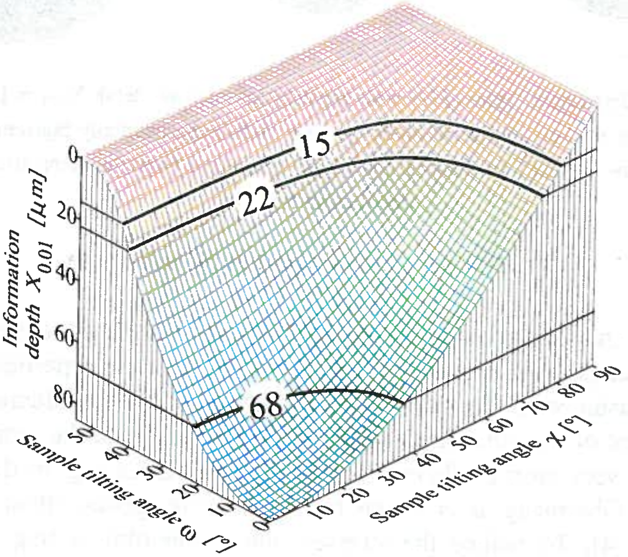

Fig. 1. The information valley (information depth $X_{0.01}$ versus titling ω and χ angles) of X-ray CoKα radiation for the *311* Bragg reflection in Al sample. The izo-depth geometrical conditions lines for registration of 15 μm and 68 μm constant-depth (*311*) pole figures are marked

Experimental verification of the method has been carried out and its effectiveness was estimated using the sample of known texture with accurately defined inhomogeneity. An example of the registered constant-depth pole figure and its processed forms are shown in Fig. 2.

The texture tomography is useful investigate tool in such problems as; anisotropy of physical properties, inhomogeneity and heredity of texture, distribution of residual stresses, fatigue wear of the constructing element surface. In spite of some limitations, the XTT adds the missing element to complete the set of the research tools of the microstructure and supplements of the electron microscopy wherever the scale of the examined phenomenon is beyond the nano-metric area.

The work presents examples of the XTT application to analysis of texture inhomogeneity of chosen FGMs due to their importance for the present-day materials engineering e.g. in the electronics and medical implantology.

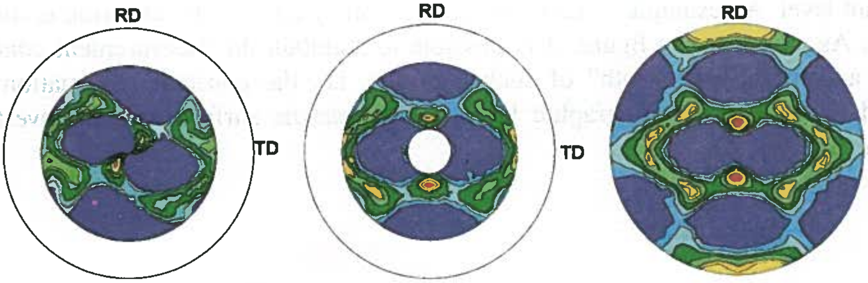

Fig. 2. Constant-depth pole figure *(111)* with constant information depth $X_{0.01} = 15\ \mu m$ for the first tomographic layer of a composite *Al* model sample: (left) experimentally registered, (centre) after transformation by the XTT procedures and (right) calculated from the reconstructed orientation distribution function

2. HfN on <111>-oriented Si substrate

FGM-made structural composites like *Si/TiN* and *Si/HfN* are applied in electronics and precision industry on account of very good electronic properties and high tribological wear resistance of the outer layer. On account of a considerable misfit of the lattice parameters of the substrate and the deposited layer, in the area of the interface boundary occur very strong inherent stresses which values e.g. in the *Si/HfN* system reach *4.5* GPa. Obviously, it is which has a disadvantageous effect on the adhesion of the layer [3, 4]. To reduce the stresses, ion bombardment (e.g. with $Si = (Si^{+})$ ions) of the substrate just before the deposition of the layer is applied. The result is the formation of a strongly defected intermediate *Si*-layer which plays the role of an area relaxing the mentioned interfacial stresses. Accordingly, a *3*-layer system is formed which properties vary along the thickness of the composite and they are closely correlated with the changes of the microstructure and the crystallographic texture. Investigation of the texture of the discussed systems requires the use of non-destructive methods, which do not disturb the subtle system of the layers structure and the existing stresses. In such case the X-ray texture tomography can also be used.

In the laboratory of the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences there has been carried out the analysis of texture of selected areas of <111>- oriented *Si* single-crystalline system with defected surface layer on which a *HfN* layer of the thickness about *500 nm* was deposited by the ion sputtering method[2].

The respective normal and constant-depth pole figures for HfN were registered by the back-reflection method of Schulz. The conventional pole figures contained data

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[2] The sample was fabricated at the Nagoya Institute of technology, Dpt. of Electrical and Computer Engineering in Japan. A layer of HfN was deposited on the surfaxce of Si-crystal with the orientation close to <111> by the technique of reactive sputtering. HfN has a regular symmetry of the crystallographic lattice (spatial group Fm3m) with the parameter $a_0 = 4.525$ Å and is of olive-brown colour. The Si/HfN sample showed orthorhombic symmetry.

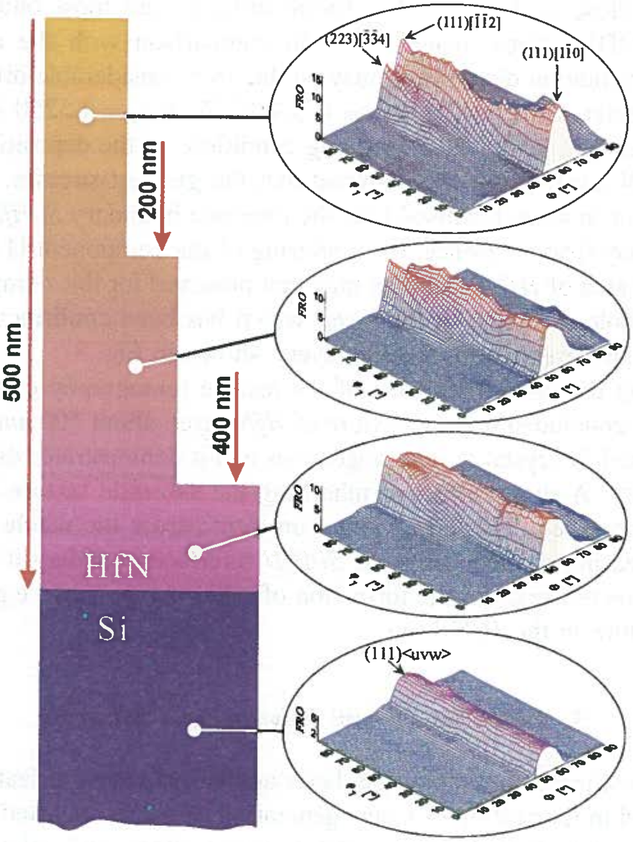

Fig. 3. Texture tomography of a HfN layer, about *500 nm* thick, deposited on <111>-oriented Si crystal, presented in the form of orientation distribution function (ODF) sections in the Euler angle space for $\varphi_2 = 45°$. The identified texture components for chosen tomographic layers of the thickness: *200 nm*, *400 nm* and *500 nm* are indicated in the figure

obtained from various information depths (about *500÷200 nm*) of the *HfN* layer depending on the Bragg's angle 2θ and the sample tilting angle χ. Constant-depth figures contained information from the tomographic layers of the thickness: $X_{0.01}$ = *200 nm*, $X_{0.01}$ = *400 nm* and $X_{0.01}$ = *500 nm*.

From the orientation distribution function (ODF) image shown in Fig. 3 it follows that the texture of the near-the-surface area has axial character with the dominating component {111}<uvw>. A comparison of the orientation distribution functions for three tomographic layers confirms the texture inhomogeneity within the deposited layer. The texture of the tomographic layer $X_{0.01}$ = *500 nm* is the nearest to the average texture, which results from its thickness comparable with the thickness of the whole deposit.

In the texture of areas more and more distant from the boundary *Si/HfN* there can be observed the components {223}<334> (dominating in the layer $X_{0.01}$ = *400 nm*) and the component close to {111}< 110 > (dominating in the most outer layer $X_{0.01}$ = *200 nm*). The ODF values increase also in comparison with the averaged texture (Fig. 3). Such orientation distribution may be due to a considerable difference between the lattice parameters of *Si* and *HfN* (a_{Si} = 5.4282 Å, a_{HfN} = 4.5250 Å), which generates internal stresses[3], or maybe, to varying conditions of the deposition of successive areas of the *HfN*-layer. It may be assumed that the greatest stresses, thus also lattice disturbance, occur in areas localised near the interface boundary *Si/HfN*, and disappear as they move away from it. Hence, the scattering of the component {111}<uvw> in the near-the-surface area of *HfN* is smaller than that observed for this component identified almost in the whole thickness of the layer, which has been confirmed by ODF cross-sections for the successive tomographic layers, shown in Fig. 3.

Summarising the obtained results of the texture tomography of a layered system *Si/HfN* it can be concluded that the texture of *HfN* layer, about *500 nm* thick, deposited on <111>-oriented *Si* crystal is inhomogeneous and it demonstrates distinct axial character {111}<uvw>. A strong effect of inheriting the substrate texture by the deposited layer has been observed. This effect is not uniform across the whole thickness of the layer. With increasing distance from the *Si/HfN* interface boundary it becomes weaker with simultaneous tendency to the formation of other components, e.g. {223}<334> of the inherent texture in the *HfN*-layer.

3. *Ti/TiN* on *Ti*- and *Polyurethane*-substrate

The X-ray texture tomography has been applied to characterization of advanced materials applied in fabrication of a new generation of a heart assisted device (artificial human heart chamber) from bio-acceptable titanium alloys, and polyurethane with the final surface made of modified nano-structure and deposited nitrogen-based (*TiN, BN*) coatings [5, 6].

Results of the XTT applied to texture analysis of a 3 *μm* thick *TiN* layer deposited on a *Ti*-substrate by means of a laser ablation technique are given in Figs 4a and 4b. Crystalline orientation of the upper part of the deposit up to 2 *μm* depth exhibit strong component {111}<110>, and in texture of the whole 3 *μm* layer dominates the {100}<010> orientation. It proofs a strong texture inhomogeneity of the *TiN* layer. Its depth-profile changes when the deposit is more and more thick. Such character of texture is determined on one hand by the substrate-inheritance (predomination of <111> axis) and on the other hand by the parameters of deposition process (predomination of < 100 > axis). The consequence of the texture inhomogeneity of the *TiN* layer is a gradient nature of its properties, like adhesion to substrate, wear- and corrosion-resistance as well as bio-compatibility.

Analogical texture analysis was performed for a 3 *μm* thick *TiN* layer deposited on a Polyurethane-substrate (*PU*-substrate). In the case the texture inhomogeneity has

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[3] The measurement of residual stresses for the same sample has confirmed their very high value, above 4.5 GPa in the HFN layer [4].

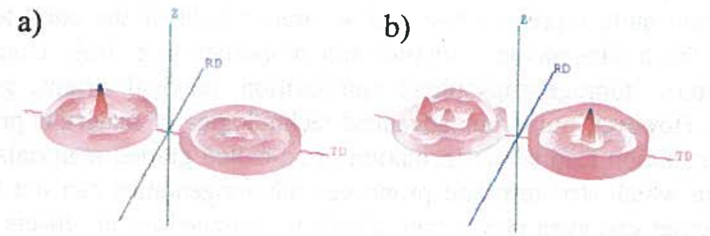

Fig. 4. (a) 3D view of the (111) constant-depth pole figures for 2 *μm* (left) and 3 *μm* (right) near-surface layers of *TiN* deposited on *Ti-* substrate. (b) 3D view of the (100) constant-depth pole figures for 2 *μm* (left) and 3 *μm* (right) near-surface layers of *TiN* deposited on *Ti*-substrate

been proved too, therewith the dominant components up to 2 *μm* depth and for the whole 3 *μm* layer were the same {112}<011> but developed to different extent (see Figs 5a and 5b). Moreover, a large size <110>-oriented *TiN*-cluster was identified at the deeper part of the deposited layer.

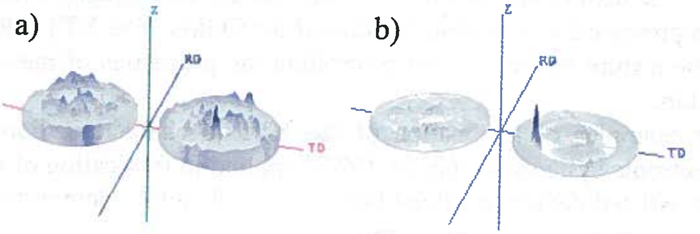

Fig. 5. (a) 3D view of the (111) constant-depth pole figures for 2 *μm* (left) and 3 *μm* (right) near-surface layers of *TiN* deposited on *Polyurethane*-substrate. (b) 3D view of the (100) constant-depth pole figures for 2 *μm* (left) and 3 *μm* (right) near-surface layers of *TiN* deposited on *Polyurethane*-substrate

4. Final remarks

Technological processes involved in production of the FGMs lead to obtaining desirable physical properties of the materials or constructing elements, and are usually focused on bringing in appropriate changes in their internal structure. In principle, such structural changes on both nano- meso- and microscale affect the increase/decrease of crystal lattice defects, the changes of grains size/shape, the modification of phase composition and phase transition, the appearing or disappearing internal stresses in the material, as well as the formation and/or modification of preferred crystallographic orientations (textures).

Usually, the structural analyses and studies of a material sample or a FGM-made structural element are carried out by means of elastic scattering techniques (mostly X-ray diffraction and electron microscopy) in which appropriately prepared sample surface or chosen sample sections are thoroughly examined. Such measuring procedures enable to obtain quite representative and accurate results if the considered material characterizes the homogeneous structure and properties (e.g. fully isotropic crystallographic texture, homogeneous phase composition, residual strains, grain sizes or morphology). However, numerous advanced technologies of materials production and elements construction lead to the formation of so-called graded materials (structurally anisotropic) in which structure and properties inhomogeneities can not be neglected, and in some cases can even play a crucial role in designed novel objects or tools with more sophisticated properties.

Recently, the modern technologies as: the bonding of the oxide ceramics (Al_2O_3 or ZrO_2) or nitride ceramics (Si_3N_4 or AlN) to metals, diffusive soldering, laser-aided depositing bio-compatible $Ti(NC)$ layers, and many others offer new possibilities in fabrication of novel materials and constructing elements with desirable structural properties and functionality. In these cases, conventional measuring techniques and investigating methods (sufficient for homogeneous materials) become not satisfactory enough and the other, more sophisticated and much more precise ones, should be developed and employed. The texture analysis by the X-ray texture tomography showed the effectiveness of the presented way of investigation of the FGMs. The XTT allows to known some extent the texture formation and controlling the properties of materials with the gradient structure.

Presented examples of application of the XTT to characterization of advanced FGMs like electronic systems *Si/HfN* or *Ti/TiN* applied in fabrication of a new generation of a heart assisted device (artificial human heart chamber) demonstrate usefulness of the presented non-invasive research tool.

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