Hardness Enhancement and Corrosion Current of Multilayer Coatings Based on Titanium Nitride

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Abstract: In this article we explore the possibilities to obtain hardness enhancement in three different types of multilayer system: TiN/AlN, TiN/NbN and TiN/TaN, produced by bias-dc magnetron sputtering under the same deposition conditions. Multilayer structure and chemical composition were confirmed by GDOES (Glow discharge optical emission spectroscopy). Crystalline structure of component layers was studied by XRD (X-ray diffraction). Microhardness was measured by using a classic Vickers microdurometer and SEM (Scanning electron microscopy), as well as, by nanoindentation. Corrosion current was determined by Tafel extrapolation method.

Key words: Multilayers, hardness enhancement, negative bias, nanocrystalline structure, interfaces.

1. Introduction

Superhard and ultrahard materials are defined [1] as those with Vickers hardness in the ranges 40-80 GPa and more than 80 GPa respectively. Since 1995, after original finding of Veprék and Reiprich [2, 3] about the hardness of nanocomposite: nc-TiN-a-Si₃N₄, an intense research on these materials has started. These materials have been produced as nanostructured coatings on high speed steel, silicon and other substrates.

Several structures have been developed for superhard and ultrahard nanostructured coatings such as: (1) nanocomposites coatings [4, 5], made for instance by co-sputtering of two or more targets in an atmosphere of argon and nitrogen; (2) nanoscale multilayers [6-8], or superlattices, where layers of titanium nitride and other nitrides with wavelengths less than 10 nm are superposed one on the top of other; (3) graded metal nitrides [9], where the relative content of two metals changes gradually in the coating.

In This paper we describe the production by dc

magnetron sputtering of multilayers based on titanium nitride on HSS (High speed steel) substrates. Specifically we report on the production of TiN/AlN, TiN/NbN and TiN/TaN multilayers. Chemical analysis of each layer was made by GDOES (Glow discharge optical emission spectroscopy). We describe also structural characterization by XRD (X-ray diffraction). Hardness was measured by using a Vickers microdurometer as well as by using nanoindentation. Electrochemical corrosion measurements are also reported.

2. Experimental Procedures

TiN/AlN, TiN/NbN and TiN/TaN multilayers were produced by dc magnetron sputtering technique. We used two sputter guns: one with a titanium target and the other one with other metal target, specifically, aluminum, niobium or tantalum. All targets were 3 inches diameter and 4 mm thick; their purity was better than 99.99%. Substrates were high speed steel. The multilayers were produced by maintaining first the substrate above the titanium target for 5 min, then rotating the substrate holder and maintaining it during

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1 min above the other-metal target; and repeating the process until we obtained twenty layers of TiN and 19 layers of the other nitride, i.e. the first and last layers are made of a titanium nitride. The process always started with sputtering a titanium adhesion layer during 2 min sputtering. During nitrides deposition, the sputter atmosphere was always 3.5×10^{-4} mbar nitrogen and total pressure (argon + nitrogen) 5.6×10^{-3} mbar. Current deposition for titanium nitride was always 600 mA and for the other nitrides 300 mA. The substrates were always heated at 400°C and biased at -100 V .

Thickness of each layer was first estimated by deposition time and previous calibration of deposition rate for each material. GDOES was used to analyze the chemical composition of each layer and verify the thickness of each layer. For that, Horiba Profiler 2 was used operating at 650 Pa and 35 W rf-power. The crystalline structure of our coatings was studied by XRD. A Phillips diffractometer Xpert 2000 with $\lambda = 0.154\text{ nm}$ from K_{α} copper transition was used in Bragg Bretano configuration. Coatings on steel were indented during 25 s, by using a Buehler microdurometer. The indented samples were then taken to a SEM (Scanning electron microscopy) equipment in where diagonal of the indentations were measured. A FEI model Quanta 650 SEM equipment providing a calibrated microscale was used. A second measurement of hardness was made by nanoindentation with a Berkovich tip, obtaining simultaneously the elastic modulus. We used multiple partial unloading indents with a maximum load of 15 mN to retrieve data at 25 depth values per indent with 16 indents per sample. Evaluation of the data was made according to the Oliver-Pharr [10] model. An Gamry-Reference 600 computer-controlled potentiostat/galvanostat/ZRA connected to a three-electrode cell was used for the measurements of electrochemical corrosion. The working electrode was the test material with an immersed area of 1.33 cm^2 , platinum and silver/silver chloride (Ag/AgCl) electrodes were used as the counter and reference

electrodes, respectively. The solution inside the reference electrode compartment was potassium chloride (KCl) with concentration of 3.0 mole/liter. The test solution was a naturally aerated 0.10 M $\text{Na}_2\text{SO}_4 - 0.01\text{ M NaCl}$ solution at room temperature (26°C). Potentiodynamic polarization curves were obtained after immersion in 0.10 M $\text{Na}_2\text{SO}_4 - 0.01\text{ M NaCl}$ solution for 1 h using a scan rate of 0.166 mV/s , from -250 mV until $+250\text{ mV}$ with respect to the OCP (Open-circuit potential).

3. Results

From deposition rate of nitrides deposited at sputter conditions mentioned in previous section, we estimated the thickness for each layer. These results are shown in Table 1.

In Fig. 1, we show the results of chemical analysis by GDOES. The multilayers structure of the three samples is very well defined. We can see 9 layers of aluminium nitride intercalated with 10 layers of TiN in Fig. 2a, 19 layers of NbN with 20 layers of TiN in Fig. 2b and 19 layers of TaN with 20 layers of TiN in Fig. 2c. There are, however, some details to explain. When the distance in the direction from the top surface of the multilayers to the substrate increases, the intensity of peaks of the metal elements decreases. This effect is known as the crater effect and it is due to the loss of resolution when depth increases [11, 12]; the continuous changes in the shape of the crater after each interface induces a higher mixing of the layers. So, quantitative information of the chemical composition and the width of layers only is reliable from the two first layers. We have obtained the thickness of a bilayer (wavelength) as the distance (in nm) between the two first peaks corresponding to the metal (Al, Nb or Ta) and the thickness of AlN, NbN or TaN layers as the width at half height of those peaks. We conclude that the chemical composition is very close to the stoichiometry of the corresponding nitrides expected and the thickness of the layers agree with those estimated in Table 1.

Fig. 1 GDOES analysis of multilayers systems (a) TiN/AlN, (b) TiN/NbN and (c) TiN/TaN on HSS-steel.

Fig. 2 X-ray diffractograms of multilayers (a) TiN/AlN, (b) TiN/NbN and (c) TiN/TaN on HSS steel.

Table1 Estimation of each-layer thickness and total thickness of nitride coatings.

	TiN thickness (nm)	AlN, NbN and TaN thickness (nm)	Number of bilayers	Total thickness (μm)
TiN/AlN	80	13	10	1.0
TiN/NbN	80	13	20	1.9
TiN/TaN	80	16	20	1.9

Fig. 2 shows XRD of a) 10 bilayers of TiN/AlN, b) 20 bilayers of TiN/NbN and c) 20 bilayers of TiN/TaN, all of them deposited on HSS-steel substrates. All the nitrides show nanocrystalline-rock-salt structure and the lattice parameters are: 0.430 nm for TiN, 0.441 nm for AlN, 0.478 nm for NbN and 0.437 nm for TaN. Grain size (D) for nanocrystalline multilayers can be estimated from broadening (B) of the diffraction lines and wavelength (λ) of the X-ray beam by the very well known Sherrer equation [13]:

$$D = \frac{0.9\lambda}{B \cdot \cos \theta} \quad (1)$$

For TiN/AlN grain size of TiN is 11.0 nm and AlN is 9.8 nm; For TiN/NbN grain size of TiN is 11.6 nm and NbN is 9.9 nm; For TiN/TaN grain size of TiN is 12.1 nm and TaN is 8.2 nm.

Fig. 3 shows SEM micrographies of Vickers indentations with loads $L = 50, 10$ and 5 gf for following samples: a) HSS-steel substrate, b) 10 TiN/AlN bilayers, c) 20 TiN/NbN bilayers and d) 20 TiN/TaN bilayers. From the size of the diagonals shown in the micrographies we have calculated the Vickers hardness which is shown in Table 2.

First, let us observe in Fig. 4 that the Vickers hardness of the HSS substrate is independent of the load in the range 100-10 gf. The value for 5 gf increases in 20%. This is a very well known indentation size effect [14] explained for the high dislocation density under the indentation tip. For large penetration depths the dislocations are distributed in larger volumes, so the dislocation density is smaller.

For the coated samples, we can observe that hardness increases noticeably for loads lesser than 50 gf and they reach high values for $L = 5$ gf. This can be explained for the very well known rule: A most real approximation to the hardness of the coating is

obtained when ratio (indentation depth/coating thickness) < 0.1 .

Considering that the values of Vickers Hardness for titanium nitride and other nitrides, components of our coatings, are in the range 1,500-2,200 kgf/mm², it is evident from our data in Fig. 5 and Table 2 that our multilayer coatings do show hardness enhancement compared to monolayer nitride coatings.

4. Nanoindentation

Hardness of our coatings was also measured by nanoindentation. The advantage of this method is essentially a smaller tip radius which allows for a more accurate measurement at small loads and low indentation depths to avoid the influence of the substrate hardness on the results. The values given in Table 3 are an average over 16 multiple-partial-unloading indents taken at an indentation depth region between 40 and 110 nm. This region enable us to get an average over several layers of the multilayered samples without interference of the substrate. At lower depths there is a large scattering of data due to the predominance of surface roughness as well as indentation tip rounding effects. The parameter H^3/E^{*2} related to toughness of coatings, is also shown.

In Fig. 4, we show graphically the hardness values obtained from data in Table 2 vs load. Data for 100 gf is also included. Table 4 shows the indentation depth in nanometers.

In Fig. 5 we show the results of multiple-partial-unloading indentation for the indents of maximum and minimum hardness.

The data show that the nanoindentation results for hardness (first row in Table 3) are consistently lower than the microhardness values measured with load $L = 5$ gf (last column in Table 2). It is very well known that

Fig. 3 SEM micrographs of 50, 10 and 5 gf-indentations on: (a) HSS substrate and multilayers, (b) TiN/AlN, (c) TiN/NbN and (d) TiN/TaN.

Table 2 Vickers hardness (kgf/mm^2).

	50 gf	10 gf	5 gf
Substrate	827	810	1022
TiN/AlN (10 layers)	1482	2670	3527
TiN/NbN (20 layers)	1262	2720	3151
TiN/TaN (20 layers)	1427	4017	4498

Table 3 Average hardness.

	TiN/AlN	TiN/NbN	TiN/TaN
H (GPa)	29.4 ± 3.4	29.7 ± 2.6	31.3 ± 1.8
E^* (GPa)	618 ± 94	635 ± 71	553 ± 40
	0.07 ± 0.03	0.06 ± 0.02	0.01 ± 0.02

Table 4 Indentation depth (nm).

	50 gf	10 gf	5 gf
Substrate	1513	682	430
TiN/AlN (10 layers)	1128	377	231
TiN/NbN (20 layers)	1367	291	246
TiN/TaN (20 layers)	1151	291	169

Fig. 4 Vickers Hardness vs load for HSS steel coated with multilayers according to inset.

there are discrepancies in hardness-measurement methods mainly due to the differences in tip geometry. Also the difference in indentation depth can have a large impact on the results. Generally, the larger indentation depth of the microhardness measurement could result in the interference of film hardness and substrate hardness, but this would lead to a lower hardness value due to the softer substrate. Also the microstructure, as well as, the intrinsic stress of the individual layers could vary during film growth. In any case, it is evident that all of our multilayer coatings show hardness enhancement. Considering the error margine, there is no significant difference in the

hardness of the three different systems.

The scattering of the hardness values is quite large (see Fig. 5). This can also be seen in data by other authors. Following the discussion by N. Pattel et al. [15], one explanation can be the polycrystalline nature of our coatings. The hardness is greater in the $\langle 111 \rangle$ -direction than in $\langle 100 \rangle$. Typically, for hardness measurements a large scattering of data is observed for samples with a high surface roughness. Since there is a difference in contact area when the tip penetrates the surface on a peak or on a valley, there will be a difference result in the hardness. Depending on the roughness this effect can be significantly larger than

Fig. 5 Maximum and minimum nanohardness as a function of indentation depth for multilayers in inset. The other data points lie between the two curves but are left out for clarity of the plot: (a) TiN/AlN, (b) TiN/NbN and (c) TiN/TaN.

Fig. 6 Potentiodynamic polarization curves of uncoated HSS steel and multilayer coated and uncoated HSS steel in 0.10 M Na_2SO_4 – 0.01 M NaCl solution.

Table 5 The values of E_{corr} and i_{corr} uncoated steel and steel coated with each of the studied type of multilayers.

	E_{corr} (V)	i_{corr} (A/cm^2)
HSS steel	– 0.350	2.64×10^{-6}
TiN/TaN	– 0.301	1.7×10^{-6}
TiN/NbN	– 0.299	2.1×10^{-6}
TiN-AlN	– 0.299	2.3×10^{-6}

the crystallographic anisotropy.

5. Electrochemical Corrosion

Fig. 6 shows polarization curves for uncoated steel and steel coated with three types of multilayers. First observation is that E_{corr} for uncoated steel is – 0.35 V and for all the coated samples is the same, approximately, – 0.30 V. The fact that E_{corr} is the same for all of our three types of multilayers can be explained because the top layer in all of them is a layer of approximately 80 nm of titanium nitride. The E_{corr} is a parameter to be considered mainly when in the surrounding of the piece of interest there is another material of very different E_{corr} . In that case galvanic pairs may be stated and destroy the piece. On the other hand, the corrosion current density (i_{corr}) is a parameter

related to microscopic currents occurring inside the piece of interest when in the medium of work or environment there exist some ionic solutions. The explanation for these microscopic currents is that due to defects of the material, there is accumulation of positive and negative charges in different points on the surface of the piece. In laboratory, i_{corr} is calculated from polarization curves according to the so called Tafel extrapolation method. Following this, we have found the values of i_{corr} for uncoated steel and steel coated with each of the studied type of multilayers described in Table 5. We can see that i_{corr} for coated samples is only slightly lesser than for uncoated samples. The minimum i_{corr} (maximum anticorrosive protection) found is for TiN/TaN multilayers. In this case current corrosion is 64% current corrosion of uncoated steel.

6. Discussion

It is very well known that negative bias voltage between – 100 and – 200 V applied to high-speed-steel substrates during coating deposition by dc or rf magnetron sputtering of titanium nitride and other

metal nitride increases noticeably the hardness of the coatings [18-20]. This hardness increasing is generally associated to changes of texture respect to no-biased substrates and the creation of high density of defects. On the other hand, superhard-multilayer coatings have been produced [21-24] by the intercalation of layers of two nitrides made also by sputtering with negative bias of the substrate. In the case of superhard-multilayer coatings, the hardness enhancement is usually explained by four mechanisms: (i) dislocation blocking [8, 25] due to the different shear moduli between two layers of different materials, (ii) the Hall-Petch effect [26] which explains the increase of hardness with decreasing grain size, (iii) alternating strain field due to the lattice mismatch [27] and (iv) enhancement of the elastic modulus [28].

In this work we have produced multilayers of TiN and MeN (where Me = Al, Nb and Ta) under the same deposition conditions, including – 100 V bias substrate. We have shown microhardness data as measured by classical Vickers microdurometer, as well as, nanohardness data measured by nanoindentation with Berkovich tip. Vickers microhardness for load $L = 5$ gf, according to column 4 of Table 2, is in the range of $3,100 \text{ kgf/mm}^2$ for TiN/NbN to $4,800 \text{ kgf/mm}^2$ for TiN/TaN multilayers, however these values correspond to individual indentations. Considering only data on Table 4 for average nanohardness, we conclude that all of our multilayer systems show hardness enhancement respect to monolayers systems and there is no significative difference among them.

In order to explain the mechanisms for hardness enhancement in our coatings, we state the following: (1) From GDOES data, it is evident that we have a multilayer structure, i.e interfaces between materials with different elastic constants [29-32], then it is possible some contribution to hardness enhancement from dislocation blocking due to different shear moduli; (2) From our XRD data, it is evident that we have very small grain size, then it is possible in our coatings some contribution to hardness enhancement from Hall-Petch

effect; (3) Lattice parameter of cubic tantalum nitride is very close to that of titanium nitride and some mismatch lattice could be expected; (4) The elastic modulus of our coatings are higher than respective monolayers so hardness enhancement could also be related to this fact.

It is not possible from our data to discriminate the specific contribution of each of the mentioned mechanisms, however, it is true that both, interfaces and grain boundaries, created by bias sputtering or mismatch, generate high defect density in the coatings. Defects hinder the movement of dislocations, thus hardening the material. That could be a basic summary for explanation of hardness enhancement in our multilayer respect to monolayers coatings.

7. Conclusions

We have produced three types of multilayer coatings by dc magnetron sputtering with substrate biased at – 100 V and with the same sputter conditions, the layers type were: TiN/AlN, TiN/NbN and TiN/TaN. The thickness of titanium nitride layer was 80 nm titanium nitride and for the other nitride layers the thickness was between 13 and 16 nm. The multilayers structure was verified by GDOES and nanocrystalline structure of each layer was verified by XRD. Microhardness and nanohardness were measured with classical Vickers microdurometer and by nanoindentation, respectively. Values of microhardness with load $L = 5$ gf result higher than nanohardness with indentation depth 100 nm. In both cases (Vickers and nanoindentation) hardness enhancement with respect to the monolayers is evident. Average nanohardness taken over 16 indentations per sample results almost the same for the three types of multilayers, approximately 30 GPa. We conclude that the mechanisms for hardness enhancement are basically the same in the three types of layers: hindering of the movement of dislocations due to the high density of defects created by interfaces and grain boundaries. Electrochemical corrosion measurements

were also carried out and the values of E_{corr} and i_{corr} are also almost the same for the three types of multilayers. So, the three types of multilayers based on titanium nitride and prepared under the same sputter conditions show similar values of nanohardness and the same electrochemical behavior independently of the partner layer: aluminium nitride, niobium nitride or tantalum nitride.

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References

- [1] Zhang, S. et al. 2003. "Nanostructured Thin Films and Coatings: Mechanical Properties."
- [2] Veprék, S. and Reiprich, S. 1995. "A Concept for the Design of Novel Superhard Coatings." *Thin Solid Films* 268: 64-71.
- [3] Veprék, S. 1999. "The Search for Superhard Materials." *J. Vac. Sci. Technol. A* 17 (5): 2401-20.
- [4] Veprék, S. and Jilek, M. 2002. "Superhard Composite Coating: from Basic Science toward Industrialization." *Pure Appl Chem.* 74 (3): 475-81.
- [5] Ribeiro, E., Mańczyk, A., Carvalho, S., Rebouta, L., Fernandes, J. V. and Alves, E. 2002. "Effects of Ion Bombardment on Properties of DC Sputtered Superhard (Ti, Si, Al) N Nanocomposite Coatings." *Surface and Coatings Technology* 151-152: 515-20.
- [6] Subramanian, B., Ananthakumar R. and Jayachandran, M. 2011. *Cryst. Res. Technol.* 46 (12): 1273-82.
- [7] Barshilia, H. C. and Rajam, K. S. 2003. *Bull. Mater Sci.* 26 (2): 233-7.
- [8] Auger, M. A., Sanchez, O., Ballesteros, C., Jergel, M., Aguilar, F. M. and Falcony, C. 2003. "TiN/AlN Bilayers and Multilayers Grown by Magnetron Co-Sputtering." *Thin Solid Films* 433 (1): 211-6.
- [9] Zeng, X. T., Zhang, S. and Hsieh, J. 1998. "Development of Graded Cr-Ti-N Coatings." *Surface and Coatings Technology* 102: 108-12.
- [10] Oliver, W. C. and Pharr, G. M. 1992. "An Improved Technique for Determining Hardness and Elastic Modulus using Load and Displacement Sensing Indentation Experiments." *J. Mater. Res.* 7: 1564-70.
- [11] Oswald, S. and Baunack, S. 2003. "Comparison of Depth Profiling Techniques Using Ion Sputtering from the Practical Point of View." *Thin Solid films* 425: 9-19.
- [12] Nelis, T. and Payling, R. 2003. "Glow Discharge Optical Emission Spectrometry." In *Surface Analysis Methods in Materials Science of Springer Series in Surface Sciences*, 23: 553-9.
- [13] Scherrer, P. 1918. "Nachrichten von der Gesellschaft der Wissenschaften Goettingen." *Mathematische-Physikalische Klasse* 2: 98-100.
- [14] Guzman, M. S., Neubauer, G., Flinn, P. A. and Nix, W. D. 1993. "Materials Research Society." *Mat. Res. Symp. Proc.* 308.
- [15] Patel, N. et al. 2014. "Secondary Hardness Enhancement in Large Period TiN/TaN Superlattices." *Surface & Coatings Technology* 254: 21-7.
- [16] McCafferty, E. 2005. "Validation of Corrosion Rates Measured by the Tafel Extrapolation Method." *Corrosion Science* 47 (12): 3202-15.
- [17] Tafel, J., Schmitz, K., Naremann, K. and Emmert, B. 1905. "Über Die Polarization bei Kathodischer der Protonuebertragung." *Z. Phys. Chem.* 50: 641-752.
- [18] Sproul, W. D., Rudnik, P. J. and Graham, M. E. 1989. "The Effects of N₂ Partial Pressure, Deposition Rate and Substrate Bias Potential on the Hardness and Texture of Reactively TiN Coatings." *Surface and Coating Technology* 39/40: 355-63.
- [19] Dudek, M., Zabeida, O., Klemberg, S. J. E. and Martinu, L. 2009. "Effect of Substrate Bias on the Micro-Structure and Properties of Nanocom-Posite Titanium Nitride – Based Films." *Journal of Achievements in Materials and Manufacturing Engineering* 37: 416-21.
- [20] Ait-Djafter, A. Z., Saolua, N., Aknouche, H., Guedouar, B. and Madaoui, N. 2015. "Deposition and Characterization of Titanium Aluminum Nitride Coatings Prepared by RF Magnetron Sputtering." *Applied Surface Science* 350: 6-9.
- [21] Ou, Y. X., Lin, J., Tong, S., Che, H. L., Sproul, W. D. and Lei, M. K. 2015. "Wear and Corrosion Resistance of CrN/TiN Superlattice Coatings Deposited by a Combined Deep Oscillation Magnetron Sputtering and Pulsed dc Magnetron Sputtering." *Applied Surface Science* 351: 332-43.
- [22] Zhang, S. H., Byon, E., Li, M. X., He, Y. Z., Cai, F. and Wang, L. 2011. "Realization of Superhard Nanocomposites with Sufficient Toughness: Superlattice Nanocrystal-TiN/Amorphous-(W, Ti) C_{0.83} Films." *Thin Solid Films* 519: 1901-6.

- [23] Zhang, S. H., Li, J. L., Chen, Z. and Li, M. X. 2012. "Realization of Superhard Chromium Nitride-Based Films: A Superlattice Nanocrystalline - Cr₂N/Amorphous - WC Film." *Thin Solid Films* 520: 4984-9.
- [24] Lin, J. L., Moore, J. J., Mishra, B., Pinkas, M., Zhang, X. H. and Sproul, W. D. 2009. "CrN/AlN Superlattice Coatings Synthesized by Pulsed Closed Field Unbalanced magnetron Sputtering with Different CrN Layer Thicknesses." *Thin Solid Films* 517: 5798-804.
- [25] Chu, X. and Barnett, S. A. 1995. "Model of Superlattice Yield Stress and Hardness Enhancement." *J. Appl. Phys.* 77: 4403-41.
- [26] Anderson, P. M. and Li, C. 1995. *Nanostruct. Mater.* 5: 349.
- [27] Kato, M., Mori, T. and Schwartz, L. H. 1980. "Hardening by Spinodal Modulated Structure." *Acta Metall.* 28: 285-90.
- [28] Cammaratta, R. C., Schlesinger, T. E., Kim, C., Qadri, S. B. and Edelstein, A. S. 1990. *Appl. Phys. Lett.* 56: 1862-4.
- [29] Chen, D. et al. 2009. *Acta Metall. Sin. (Engl. Lett.)* 22 (2): 146-52.
- [30] Gerlich, D., Dole, S. L. and Slack, G. A. 1986. "Elastic Properties of Aluminum Nitride." *J. Phys Chem Solids* 47 (5): 437-41.
- [31] Chang, J. et al. 2012. *J. Appl Phys.* 112 (8): 0835519.
- [32] Dahua, R. et al. 2014. "Advanced Materials." *Journal of Wuhan University of Technology Mater. Sci.* 29: 49-57.