

## POSSIBILITIES OF HARDNESS MEASUREMENT OF COMPOSITE COATING BASED ON PTFE WITH $Al_2O_3$ PARTICLES APPLIED ON ALUMINIUM SUBSTRATE

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**Abstract.** The importance of surface treatment is emphasized by new knowledge from the preparation of coatings and thin films. These coatings can influence basic properties, such as corrosion resistance, surface friction characteristics, hardness and many others. This paper pays attention to the evaluation of the hardness of the polytetrafluoroethylene-based composite coating with the addition of micro and nano aluminium oxide particles at various concentrations. The experiment describes the testing of composite coatings PTFE +  $Al_2O_3$  at concentrations of  $0.1\% \cdot l^{-1}$ ,  $0.01\% \cdot l^{-1}$ ,  $0.001\% \cdot l^{-1}$  by various methods of hardness measurement and their evaluation by SEM. The hardness of the coating thus prepared was influenced by its thickness. For measurements the nanoindentation test and Vickers hardness test were used. The measurement results were also influenced by the chosen coating technology, which influenced the uniformity of the distribution of particles in the coating. To verify the uniformity of the particles in the evaluation of individual samples the SEM analysis was used. The distribution of particles in the coating has the effect of influencing the properties of the coating, not only the hardness, but also, for example, the abrasion resistance, roughness etc. The most suitable method for evaluating the hardness of a tested coating is the nanoindentation test, which has proved to be the most suitable method. Values are influenced by the injection point, i.e. whether there was an  $Al_2O_3$  cluster or only a Teflon coating in the area. We confirmed the assumption of uneven distribution of particles and their aggregation using electron microscope documentation. The experimentally verified results are discussed at the end of this paper and there are given individual conclusions and recommendations.

**Keywords:** PTFE,  $Al_2O_3$ , hardness measurement, composite coating, aluminium substrate.

### Introduction

The trend of the present industrial age is the effort to achieve the high quality of produced products with the highest utility properties and, at the same time, the effort to achieve the highest possible economics of the product itself with respect to environmental and other aspects of the production, and also on the product itself. The technology of surface treatment of materials, which has been the subject of continuous and, recently, stormy development, helps meet these requirements of modern industry.

For the species diversity, wide applicability to the varying range of materials, with the possibility of achieving the different desired properties, today the surface treatment technologies are at the forefront in the design of new products. Over time, surface treatment technology has gained the same position in product design, as well as in the choice of materials according to their properties. Correctly selected surface treatment in conjunction with suitably selected base material results in the achievement of synergistic properties of a surface-treated material, or the product made as a complex. The surface treatments thus help increase the service life of the products, and also, for example, in the marketing, promotion of the product itself.

In general, coatings and protective coatings are widely used. Most often they are formed on the surface of the material to improve the properties of the material, such as wear resistance, reduction/increase of the friction coefficient, corrosion protection, electrical properties and/or mechanical properties. The basic mechanical properties include hardness [1].

We need to know these properties for comfortable use of these materials for various purposes. Hardness can be divided into three basic groups – hardness, microhardness and nanohardness. Individual tests differ in load and technology. An example of hardness rating is the use of Brinell measurements on aluminium materials. In this case, the resulting values range from 15 HBW for pure aluminium up to 140 HBW for hard Al alloys with high strength [2].

Hardness tests are among the so-called destructive. The basic principle is to load the specimen by pressing in a test specimen with a specified geometry of the shape, given a force for a certain time. The hardness parameter is not physically defined, as it depends on many different factors. For example, the Brinell test hardness value is the result of the character and the voltage depending on the size of the force.

Hardness tests can be divided into several aspects. One of which is, for example, the above-mentioned load. The most commonly used measurement methods are according to Brinell (the size of the indentation indenter shaped beads and loading forces are calculated as the resulting values, suitable for soft and medium-hard materials), according to Rockwell (this method does not measure the size of the impression, but is read directly on the hardness tester, the shape of the indenter is either a ball or a diamond cone, suitable for soft and very hard materials), according to Vicker (the test specimen is a regular quadrilateral pyramid, the method is suitable for soft and very hard materials), according to Knoop (the impression is in the shape of a diamond with a diagonal ratio of about 1: 7, the test piece is a diamond pyramid with a diamond base).

Another type is according to the method of loading the tested material, which can be divided into static and dynamic. Static methods include all the above tests, where the test specimen is gradually injected with increasing force into the tested material. Static tests are simple and therefore often used. In dynamic methods, the indenter penetrates into the tested material by impact. This type of test is also referred to as impact. This group includes, for example, the Marten's test (a diamond cone is drawn over the surface of the test specimen, with a gradually increasing force and an apex angle of 90 ° and a tip radius of 0.2 mm, the resulting value is determined at the moment, when a 0.1 mm thick scratch is formed or the same load is repeated, and the width is subsequently compared).

In this case, it is necessary to choose a method and load suitable not according to the type of the base material, but according to the type of coating. For measuring coatings, it is suitable to use microhardness measurement by Vicker's or Marten's method. In this type of coating it is however preferable to use measurement of nanohardness, e.g. indenter Berkowich type.

Nowadays, there are more and more requirements for the surfaces, but the base material itself is not able to satisfy them. Therefore, there are applied layers and coatings on the surface of the base material (substrate). The surface of the substrate is pre-treated before the application of the final surface treatment, either by phosphating or by anodizing (anodic oxidation). These types of treatments are known as conversion coatings. Individual pre-treatments have their advantages and disadvantages and, of course, different application possibilities [3].

By the surface layers, coatings and films themselves can (among other properties) be evaluated the hardness, but on a different scale – micro and nano hardness. Evaluation of the hardness of the coating is complicated in many ways. For example, when measuring Vickers hardness, we can define 2 basic problems. The first is the coating thickness, which is never completely uniform. For this method of measurement, the coating thickness must be ten times greater than the indentation depth (as determined by ČSN EN ISO 6507-1). This is also related to the second problem, the test load applied to the coating itself [1]. To eliminate these effects, the hardness was measured using a nanoindentation test.

Among the coatings used to improve the properties of the materials there are, for example, PVD coatings, chemical coatings, such as sol-gel zirconium nanopassivation (Fig. 1), amorphous carbon DLC or TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, WC, etc. coatings. All these coatings exhibit all of the following properties, or a combination, thereof: high hardness, corrosion resistance and very high adhesion resistance (repellency).

In recent years, composite coatings recorded significant development. These coatings can be divided into 4 basic groups:

- organic/inorganic composite coating (matrix/filler),
- organic/organic composite coating,
- inorganic/organic composite coating,
- inorganic/inorganic composite coating [4].

The composite coatings consist of two materials (phases) separated from each other by the interface area. The main component is a matrix and minor filler. These types of coatings can be viewed from several points of view, such as the matrix type or filler type. Both of these components affect the basic properties. In this paper, the research is focused on the PTFE matrix and dispersed filler of micro and nano alumina particles (Al<sub>2</sub>O<sub>3</sub>). However, other materials can also be used to form coatings. The polymeric material can be polyurethane, epoxide, polyethylene glycol (PEG),

polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polystyrene, polyacrylate, polyester, polyamide, etc. Methods, including CVD – chemical vapour deposition, are used for inorganic matrix (metal or alloy matrix), thermal plasma spraying, powder metallurgy, PVD – physical vapour deposition [5].

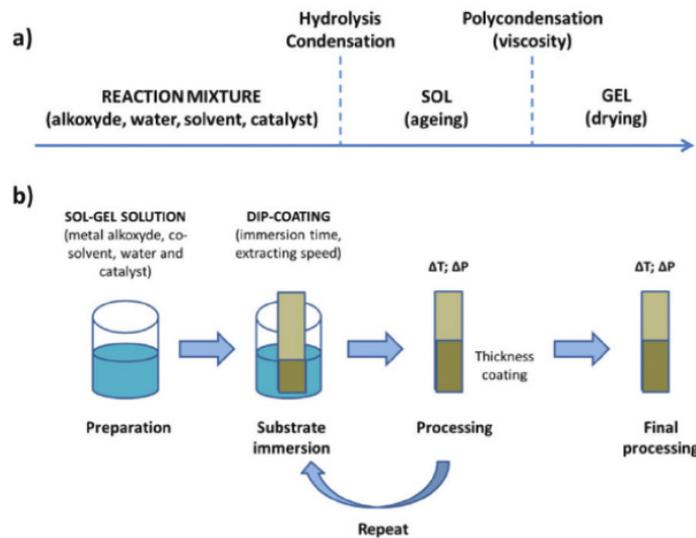


Fig. 1. Sol-gel method scheme [6]

PTFE (polytetrafluoroethylene) was used as the matrix and particles (micro and nano size) of  $\text{Al}_2\text{O}_3$  were selected as filler in the experiment that is the subject of this paper. The reason for using  $\text{Al}_2\text{O}_3$  is its good properties, which could increase the utility properties of PTFE coating.  $\text{Al}_2\text{O}_3$  is a refractory oxide with low cost, superior hardness, and high resistance to oxidation and corrosion at high temperature [7]. However, other particles such as  $\text{TiO}_2$ , WC, ZnO,  $\text{CaCO}_3$  can also be added to this type of coating.

The coating technology itself is known as the dip coating technology. This technology is one of the most commonly used in industrial practice and is accomplished by soaking the base material in a coating bath, followed by removal from the bath while maintaining a constant speed and strict control of bath parameters (temperature, pH, purity/chemical composition). Depending on the selected rate of removal from the bath, we achieve the desired coating properties of the base material. This process is controllable, that means, we can achieve (for example) a thinner coating layer using a high removal rate and a thicker coating layer using a slower removal rate subject to certain parameters and conditions. In this technology, the individual micro and nanoparticles are dispersed in the prepared solution – bath and then adhere to the final coating formed on the substrate after removal from the coating bath. During the coating process, the bath is necessarily constantly agitated to avoid sticking of the particles. The specific method of coating we have chosen is shown in Figure 2.

### Experimental Part – Technology

The composite coating was applied to an Al-Si type aluminium alloy substrate. Specifically, it was AlSi10Mg. It is a common commercial alloy with the chemical composition: Al (balance), Si (9.0 – 11.0 wt. %) Fe ( $\leq 0.55$  wt. %) Cu ( $\leq 0.05$  wt. %) Mn ( $\leq 0.45$  wt. %) Mg (0.2 – 0.45 wt. %) Ni ( $\leq 0.05$  wt. %) Zn ( $\leq 0.10$  wt. %) Pb ( $\leq 0.05$  wt. %) Sn ( $\leq 0.05$  wt. %) Ti ( $\leq 0.15$  wt. %).

The aforementioned composite coating composed of polytetrafluoroethylene (PTFE) and aluminium oxide ( $\text{Al}_2\text{O}_3$ ) was applied on the surface of the Al substrate. The filler was applied at various concentrations. The cross-section of the experimental coated sample is shown in Figure 3. The thickness of the coating is in the range of 10 – 25  $\mu\text{m}$ . The experimental samples were labelled as follows: **1** – PTFE coating, **2A** – PTFE coating + 0,001 %  $\text{Al}_2\text{O}_3$ , **2B** – PTFE coating + 0,01 %  $\text{Al}_2\text{O}_3$ , **2C** – PTFE coating + 0,1 %  $\text{Al}_2\text{O}_3$ .

The coating process is as follows: the first step of the coating technology is alkaline degreasing applied at an elevated temperature of 50-60 °C. After alkaline degreasing, zirconium nano passivation was used, and this type of pre-treatment works at room temperature. The thickness of this layer is around 30 nm. The experimental samples were dried in the dryer with forced air circulation at 150 °C 15 minutes. After this operation, the composite coating was applied. This step contains the preparation of the liquid bath – PTFE + Al<sub>2</sub>O<sub>3</sub> particles in the selected ratio. Thus prepared coating was dried in the dryer with forced air circulation at 100 °C 30 minutes. The coating baths were prepared with a defined amount of chemicals into demineralized water. Time for each technology is different from 2 to 5 minutes for alkaline degreasing and zirconium nano passivation, and 15 minutes for PTFE + Al<sub>2</sub>O<sub>3</sub>.

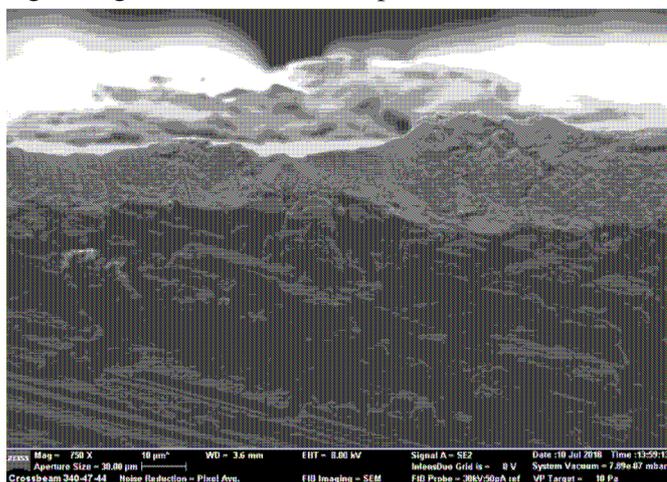


Fig. 2. Cross-section through composite coating

**Experimental Part – Measurement**

The Vickers hardness test and nanoindentation test according to Berkovich were used to evaluate the hardness of the coatings.

Vickers hardness measurement – in this case, the samples were measured according to ČSN EN ISO 6507-1 with the parameters for measurement: HV10 – 10 kp for 10 s. The measured values are shown in Table 1 and graphically shown in Fig. 3. Each measurement was repeated 3 times for 10 samples. The table shows the average values.

Table 1

**Vickers hardness test values – composite coating PTFE + Al<sub>2</sub>O<sub>3</sub> (different concentrations)**

Sample	1	1A	1B	1C
Concentrations Al <sub>2</sub> O <sub>3</sub> in the PTFE solution, % per litre	0 %	0.01 %	0.1 %	0.001 %
Ø value of the hardness HV	152.0	189.0	187,0	156,6
Standard deviation	14.75	25.61	32.53	16.15

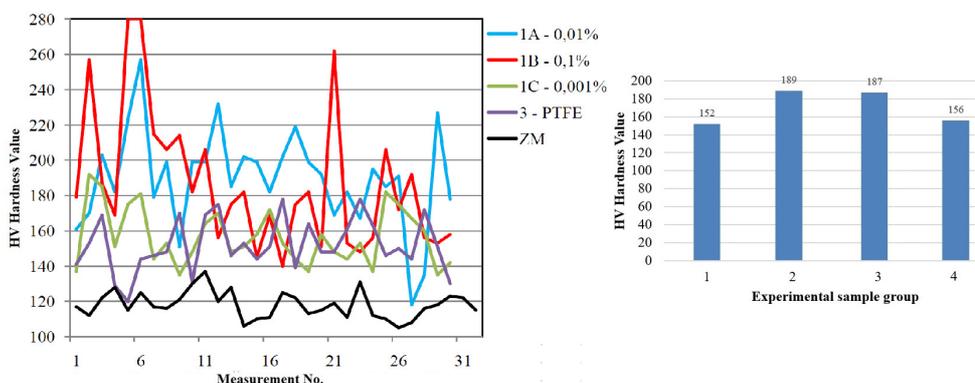


Fig. 3. Vickers hardness measurement – comparison of hardness values

The measured hardness values show large deviations. Sample 2C (PTFE + 0.1 %  $\text{Al}_2\text{O}_3$ ) shows the largest deviations. The standard deviation, in this case, is 32.50. In contrast, sample 2A (PTFE + 0.001 %  $\text{Al}_2\text{O}_3$ ) shows the lowest variance with a standard deviation of 16.15. The lowest standard deviation of all samples was found in the base material of 5.93. The higher standard deviation for samples with  $\text{Al}_2\text{O}_3$  is due to uneven distribution of particles in the coating. This fact is pointed out by the following EDX analysis. Even with this measurement, a partial puncture of the coating occurred and thus the resulting hardness of the base material was affected. Due to the not entirely suitable, convincingly interpretable Vicker's measurement results, we subjected the experimental samples to a nanoindentation test. This test is performed by making a die matrix, Fig. 4. During the measurement, 10 x 10 indentations were made with a gap of 35  $\mu$  in each axis using the Berkovich indenter, Fig. 4. The load was 5 mN.

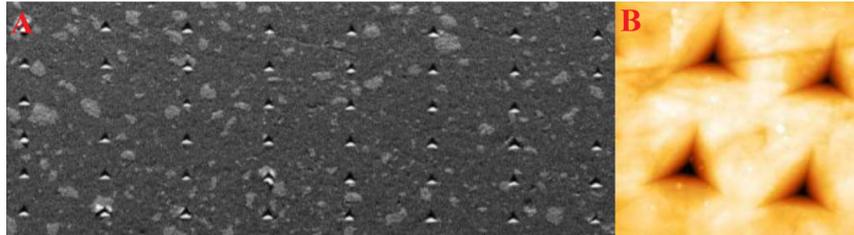


Fig. 4. Nanoindentation test – injection matrix (A), injection with Berkovich indenter (B)

The nanoindentation test was performed in two steps. The first step was to measure the hardness of the base material (uncoated) to subsequently compare the results of the experimental samples with the coating, the coating without the particles and after application of the  $\text{Al}_2\text{O}_3$  particles into the coating.

The sample had to be polished before measurement, because its surface showed high roughness after cutting, which could affect the measurement results. The second step was a measurement on the PTFE coated sample without the particles and the samples with a different concentration of  $\text{Al}_2\text{O}_3$  particles. The obtained values of nano hardness are in Table 2.

The measurement was performed with an indenter load from zero to 5 mN. This was followed by a four-second load. Then the indenter was relieved to 80 % and the thermal drift was corrected, the indenter was relieved and moved to the next position. This procedure was repeated on the entire matrix until the sample was finished and removed.

Table 2

Nanoindentation test results

Sample	Basic material	1	1A	1B	1C
Concentrations $\text{Al}_2\text{O}_3$ in the PTFE solution, % per litre	-	0 %	0.01 %	0.1 %	0.001 %
Ø measured values, GPa	1.030	1.517	1.435	1.557	0.990
Standard deviation, GPa	0.550	1.199	1.007	1.504	0.888

The values obtained by this measurement are, like in previous measurements, affected by the particles in the coating. Samples with a concentration of 0.1 %  $\cdot \text{l}^{-1}$   $\text{Al}_2\text{O}_3$  in solution show the highest value, Table 2. On the contrary, the lowest values are for the base material and for the composite coating with a content of 0.001 %  $\cdot \text{l}^{-1}$   $\text{Al}_2\text{O}_3$ . A graphical representation of the measurements is shown in Fig. 5. Measured values are heavily influenced by the clustering of particles  $\text{Al}_2\text{O}_3$ .

Because of the large variance in the measured values, we completed the research with the evaluation of composite coatings by scanning electron microscopy (SEM), Fig. 6. Using SEM, it was documented that the  $\text{Al}_2\text{O}_3$  particles were retained in the coating and confirmed the assumption of hardness measurement, i.e. uniform particle distribution and agglomeration.

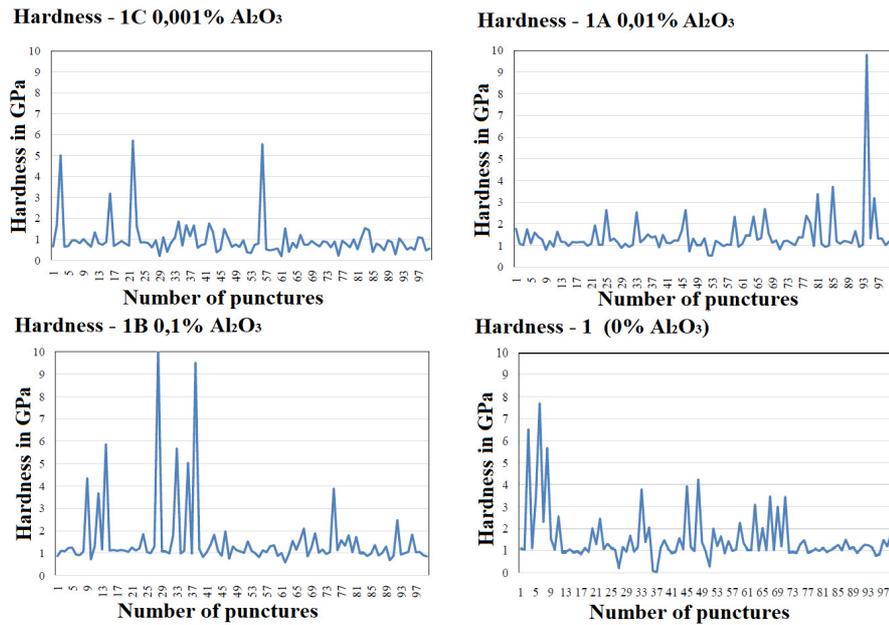


Fig. 5. Nanoindentation test – measurement results

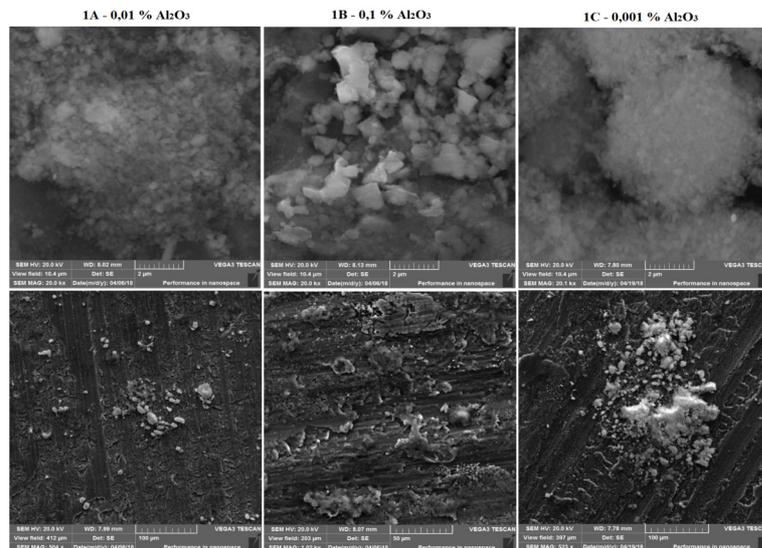


Fig. 6. SEM results

**Conclusions**

The experiment describes the testing of the composite coating (PTFE + Al<sub>2</sub>O<sub>3</sub> in the concentration of 0.1 %, 0.01 % and 0.001 % of particles per litre of solution), two different methods of hardness measurement and evaluation by SEM.

1. Measurement by the Vicker’s method – it can already be concluded from the results that the measured values have a high standard deviation, which indicates an unevenly deposited coating.
2. The method (Vicker) is not suitable for the measurement. Many indentations have pierced the coating and the hardness of the base material was measured. In addition, the standard deviation is too high. There was also a problem with “reading,” the indent. We had to choose such a load to see the indent and measure it.
3. Nanoindentation test – values are influenced by the injection point, i.e. whether there was an Al<sub>2</sub>O<sub>3</sub> cluster in the area, or only a PTFE coating.
4. When comparing the results of the nanoindentation test samples with each other, the 1A sample with 1.435222 GPa and a standard deviation of 1.007387 has the best results. This sample showed the most uniform surface and uniform measured values.

The assumption of not evenly uniform particle distribution and their aggregation was confirmed at the end of the paper using the electron microscope surface documentation. Based on the obtained results, we can conclude that the properties of the composite coating are mainly influenced by the distribution of particles in the matrix. It is, therefore, necessary to pay attention to their more even distribution and to adapt it to the coating technology.

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### References

- [1] Iost A., Bigot R. Hardness of coatings. *Surface and Coatings Technology*, Vol. 80, 1996, pp. 117-120.
- [2] Dušek J. Tvrdost, mikrotvrdost a nanotvrdost – čisté kovy měřené metodou DSI (Hardness, microhardness, nanohardness – pure metals measured by DSI method), Ph.D. Thesis. Masarykova univerzita v Brně, 2008. (In Czech)
- [3] Wang Q., J., Chung Y. *Encyclopedia of tribology*. Springer US, 2013, p. 4.139.
- [4] Phuong N., Tuan A., Pascal C., Cuong N., X. Properties and Application Nanocomposite Coatings: Preparation, Characterization. *International Journal of Corrosion*, Hindawi, Vol. 2018, p. 19.
- [5] Rajput N. Methods of Preparation of Nanoparticles – A Review. *International Journal of Advances in Engineering & Technology*, Jan. 2015.
- [6] Rivero, P., J., Goicoechea, J., Arregui, F., J. Localized Surface Plasmon Resonance for Optical Fiber-Sensing Applications. *Nanoplasmonics – Fundamentals and Applications*, June 2017.
- [7] Zhu S. G., Qu H. X., Ouyang C. X. *Advances in Ceramic Matrix Composites*, 2014, pp. 190-217.