Materials analyses of composite coatings with selected fillers

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Abstract. This article focuses on the selection of fillers for composite coatings according to their key properties, sample composition and particle morphology. Properties that we want to improve with coatings are especially durability, abrasion resistance and heat resistance. TiO₂, Al₂O₃, WC and W were selected as suitable materials. XRD and XRF analysis was performed on selected fillers to determine the exact composition and crystallographic structure. Furthermore, the samples were milled in a ball mill, sieved according to the size of the fraction and SEM analysis was performed for each fraction to determine the particle morphology.

1. Selected materials and basic properties
Coating of metallic and non-metallic materials with composite coatings is intended to improve their mechanical properties and thereby increase their service life and utility value. It is therefore very important to choose the right matrix and functional filler.

PTFE emulsion, which has already proven itself in previous research [1], [2], geopolymer substances and PMMA [3], [4], will be used as the matrix of composite coatings.
The functional filler in the form of powder was chosen according to its properties for a particular type of use of the given component (material) in order to achieve an improvement of the required properties (improved abrasion resistance, increased temperature resistance, reduced thermal conductivity...). Four materials were selected as a filler.

- TiO₂ – this metal oxide has proven itself in previous research for its advantageous properties such as UV resistance, hydrophobic and antistatic properties, abrasion resistance, etc., high hardness [4], [5]. Examples of possible applications include: increasing component life, improving abrasion resistance, improving surface non-adhesion, improving UV resistance.
- Al₂O₃ – heat resistant, hard, low thermal conductivity. Examples of possible applications: increasing the service life of the component, improving wear resistance, improving the mechanical properties.
- WC – heat resistant, hard, good electrical conductivity [2]. Examples of possible applications are: increasing component life, improving abrasion resistance, increasing heat resistance (heat shields).
- W – high melting point, high hardness, heat resistance. Examples of possible applications include: increasing component life, improving abrasion resistance, increasing heat resistance (heat shields).
By a suitable combination of matrix and functional filler, it is possible to form a composite that improves the desired property. It is also possible to apply multi-layer composite systems (for example, a high temperature undercoat and a wear resistant topcoat). Another important variable affecting the resulting properties of the composite coating is the weight concentration of filler particles in solution. In previous researches, concentrations of tenths of percent to units of percent were chosen [1], [2], [3], [4]. If the concentration is too high, the individual particles are not firmly anchored in the coating and are dropped by rubbing at very low pressure (swipe). Conversely, if the concentration is too low, the particles in the coating are not sufficient to exhibit their beneficial properties (further research will be conducted with appropriate concentration of filler particles).

The choice of particle fraction size (and their morphology) is another variable affecting the resulting properties, see chapter 3. There is also a choice of many methods of applying a composite coating to a component, which also affects the resulting surface quality and properties. The coating can be applied, for example, by dipping, brushing, sputtering, etc.

2. XRD and XRF analysis

XRD analysis was performed on a Panalytical X’Pert PRO diffractometer. The measurement was performed in a symmetrical Bragg-Brentan arrangement, which is used for standard powder diffraction. A Cu cathode X-ray lamp was used. The measured diffractograms were evaluated using HighScore Plus software with PDF-2 database. The result of XRD analysis is presented as a diffraction pattern with commentary.

XRF analysis was performed on a WDXRF instrument Rigaku ZSX Primus 4. Data were evaluated by a non-standard method of fundamental parameters, which allows the determination of elements in the range of F-U in concentrations from hundredths ppm to 100 %. The result of the XRF analysis is presented in the table (due to the large amount of other elements and oxides contained in the samples at very low concentrations, only those with a proportion greater than 0.2 % were selected for the tables).

- TiO$_2$

| No. | Component | Result | Unit | Det. Limit | El. line | Intensity | w/o normal |
|-----|-----------|--------|------|------------|----------|-----------|------------|
| 1   | TiO$_2$   | 99.8%  | %    | 0.02068    | Ti-KA    | 784.3756  | 97.4513    |

**Table 1.** XRF analysis of TiO$_2$.

![XRD analysis of TiO$_2$.](image)

**Figure 1.** XRD analysis of TiO$_2$. 


The sample contains TiO$_2$ in the form of rutile.

- Al$_2$O$_3$

**Table 2. XRF analysis of Al$_2$O$_3$.**

| No. | Component | Result | Unit | Det. Limit | El. line | Intensity | w/o normal |
|-----|-----------|--------|------|------------|----------|-----------|------------|
| 1   | Al$_2$O$_3$ | 88.6%  | %    | 0.04815    | Al-KA    | 90.4043   | 71.4467    |
| 2   | TiO$_2$   | 4.23%  | %    | 0.04847    | Ti-KA    | 1.3127    | 3.4149     |
| 3   | SiO$_2$   | 3.34%  | %    | 0.01194    | Si-KA    | 1.4998    | 2.6945     |
| 4   | CaO       | 1.30%  | %    | 0.00755    | Ca-KA    | 1.0570    | 1.0468     |
| 5   | Fe$_2$O$_3$ | 0.990% | %    | 0.00913    | Fe-KA    | 2.9819    | 0.7982     |
| 6   | MgO       | 0.425% | %    | 0.02924    | Mg-KA    | 0.1741    | 0.3427     |
| 7   | K$_2$O    | 0.310% | %    | 0.00871    | K-KA     | 0.2393    | 0.2501     |

**Figure 2. XRD analysis of Al$_2$O$_3$.**

The main crystallographic phase in the sample is Al$_2$O$_3$. The sample contains small amounts of valerite and K$_2$MgSiO$_4$.

- WC

**Table 3. XRF analysis of WC.**

| No. | Component | Result | Unit | Det. Limit | El. line | Intensity | w/o normal |
|-----|-----------|--------|------|------------|----------|-----------|------------|
| 1   | W         | 86.3%  | %    | 0.02687    | W-LA     | 1583.9812 | 88.4235    |
| 2   | Co        | 6.16%  | %    | 0.00611    | Co-KA    | 225.3081  | 6.3119     |
| 3   | Ti        | 6.10%  | %    | 0.01478    | Ti-KA    | 19.9021   | 6.2456     |
| 4   | Cr        | 0.292% | %    | 0.00834    | Cr-KA    | 2.8675    | 0.2990     |

**Figure 3. XRD analysis of WC.**

The sample contains only WC. XRF analysis does not directly determine the content of light elements (eg, C, H, N) in the compound. The content of the light elements is then calculated by software. For this sample, however, the program was unable to calculate the carbon content (probably because of
the high content of other heavy elements) and therefore is not represented in table 3. The tungsten carbide is shown further from the XRD analysis of figure 3.

- W

| No. | Component | Result | Unit | Det. Limit | El. line | Intensity | w/o normal |
|-----|------------|--------|------|------------|----------|-----------|------------|
| 1   | W          | 98.1   | %    | 0.03829    | W-LA     | 729.1112  | 86.9326    |
| 2   | Cu         | 0.767  | %    | 0.00872    | Cu-KA    | 16.8511   | 0.6793     |
| 3   | Fe         | 0.295  | %    | 0.00764    | Fe-KA    | 3.0183    | 0.2612     |

Table 4. XRF analysis of W.

Figure 4. XRD analysis of W.

The main crystallographic phase in the sample is W. The sample further contains a small amount of tungstite.

3. Particle morphology
The samples were prepared (ground) in a planetary ball mill. They were then screened for size fractions

- < 20 µm
- 20 – 40 µm
- 40 – 80 µm
- > 80 µm

and subjected to SEM analysis.

The morphology of the particles milled in a ball mill is mostly sharp-edged, as confirmed by the SEM analysis in Figures 5 – 8 for the samples tested. The particle morphology also affects the properties of the coating. The sharp-edged particles can better hold the composite matrix and will not tear (for example, abrasion) than round or spherical.

- TiO₂

Figure 5. Morphology of TiO₂ particles.

Figure 5 shows the morphology of the individual TiO₂ fractions. The particles are irregular, sharp-edged and aggregates can be seen at a fraction > 80 µm.
• **Al₂O₃**

Figure 6. Morphology of Al₂O₃ particles.
Figure 6 shows the morphology of the individual Al₂O₃ fractions. The particles are irregular, sharp-edged. Aggregates are not present.

• **WC**

Figure 7. Morphology of WC particles.
Figure 7 shows the morphology of individual WC fractions. As an input sample, a powder was used, which was produced by the spraying method, which produced spherical particles that could be observed for a fraction > 80 µm. For the other fractions, which were already formed by mechanical milling in a ball mill (from the original sample with spherical particles), we observe again an irregular shape, but not as sharp as in the previous samples.

• **W**

Figure 8. Morphology of W particles.
Figure 8 shows the morphology of the individual W fractions. The particles are irregular, acute and flaky.
4. Conclusions

Composite coatings can extend the life of a component several times and significantly improve the surface properties, thus saving costs and time. In the following research, we will look at the development of coatings that will improve the durability, abrasion resistance and heat resistance of a component. For this reason, TiO₂, Al₂O₃, WC and W materials have been selected as fillers that meet these requirements. The tested PTFE emulsion, PMMA and geopolymer materials will be used as matrix.

We determined the exact composition and crystallographic phases of selected fillers by XRD and XRF analysis. Next, we ground the samples in a planetary ball mill and sorted according to fractions. Selected fractions were subjected to SEM analysis to determine the morphology of the particles, which is irregular and sharp-edged, except for WC input material, where the particles are spherical due to the production method used.

Acknowledgements

Supported by the OP VVV Project Development of new nano and micro coatings on the surface of selected metallic materials - NANOTECH ITI II., Reg. No CZ.02.1.01/0.0/0.0/18 069/0010045.

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