Chemical Analysis of Friction Composites Used in Automotive Brake Systems Using Energy Dispersive XRF Method

Chemická analýza třecích kompozitů používaných v brzdových systémech automobilů, využívající energodisperzní XRF metodu

doc. Ing. Vladimír Tomášek, CSc.; **Ing. Barbora Thomasová, PhD.**; **prof. Ing. Jana Seidlerová, CSc.**; **Ing. Marie Kociánová**

VŠB – Technical University of Ostrava, Nanotechnology Centre, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

The method of direct chemical analysis of friction composites used in automotive brake systems using energy dispersive X-ray fluorescence spectrometry (EDXRF) was developed. Seven reference materials (RM) of friction composites with different composition simulating wide scale composition of commercial brake linings were prepared. Structure and distribution of individual components in RM were studied by scanning electron microscope with X-ray spectrometer. These parameters are similar to those of commercial brake linings. To assess the homogeneity in the whole RM volume, the top and the bottom of pellets were analyzed by EDXRF and X-ray intensities of chosen elements were compared. To get satisfactory results, prepared pellets were ground down on both sides by approx. 0.3 mm. Homogeneity of RM was sufficient after this operation. To assess the homogeneity of the surface of RM, every pellet was analyzed in seven different places and seven times in one position. Relative standard deviations (RSD) of the measured intensities of chosen elements were compared. RSD of intensities measured in seven positions were approx. twice as high as that for the measurements in one position but they still did not exceed the 3% for most of the monitored elements. Homogeneity of RM was sufficient and they were used for calibration of EDXRF spectrometer. The accuracy of the calibration model was verified by the analysis of the prepared RM using the new method. The results were satisfactory and the method is suitable for the given purpose.

***Key words**: frikční kompozity; brzdové obložení; prvková analýza; rentgenová fluorescenční spektrometrie*

Byla vyvinuta metoda přímé chemické analýzy frikčních kompozitů používaných v brzdových systémech automobilů s využitím energiově disperzní rentgenové fluorescenční spektrometrie (EDXRF). Bylo připraveno sedm referenčních materiálů (RM) frikčních kompozitů různého složení, simulujících širokou škálu složení komerčních brzdových obložení. Struktura a distribuce jednotlivých složek RM byla studována pomocí řádkovací elektronové mikroskopie s ED rentgenovým spektrometrem. Tyto parametry byly podobné komerčním brzdovým obložením. K posouzení homogenity RM v celém objemu byly analyzovány RM metodou EDXRF na horní a spodní straně pelety a výsledky byly porovnány. Připravené RM byly obroušeny z obou stran cca o 0,3 mm k eliminaci případných segregací jednotlivých složek během lisování. Homogenita RM byla vyhovující pro daný účel. K posouzení homogenity na ploše RM byly pelety analyzovány v sedmi různých pozicích a sedmkrát v jedné pozici. Byly porovnány relativní standardní odchylky (RSD) naměřených intenzit pro zvolené prvky. RSD intenzity naměřených v sedmi pozicích byly cca dvakrát vyšší než při měření v jedné pozici, ale pro většinu stanovovaných prvků nepřevýšily 3 %. Homogenita RM byla vyhovující a byly použity pro kalibraci EDXRF spektrometru. Správnost kalibračního modelu byla ověřena analýzou připravených RM s použitím nové metody. Výsledky byly uspokojivé a metoda je vhodná pro daný účel.

***Klíčová slova**: friction composites; brake lining; elemental analysis; X-ray fluorescence spectrometry*

Friction composite materials used in automotive brake systems typically consist of 20 to 30 components in a variety of mechanical and chemical properties. Phenol-(-cresol)-formaldehyde resins are used as a binder. Fibrous materials of various types (mineral, metal, aramid, carbon) are used for hardening the resin matrix. To achieve optimum friction properties, friction modifiers are used for the manufacture of brake linings. To increase the friction coefficient, abrasive materials (alumina, silica, chromite, zircon, silicon carbide) are added. To reduce brake wear, solid lubricants, such as graphite and other carbonaceous materials, and some natural sulfides (stibnite, galenite, molybdenite, sphalerite, pyrite, chalcopyrite) are added. Metallic chips, fibers or powders (copper, brass, bronze, tin) are added to remove heat from the friction surface. Further components, such as barite, calcite, magnesite, dolomite, MgO, CaO, ZnO, clay minerals and other materials are added so that the final product is cheaper while maintaining all its functional properties. [1 – 7]

From the review of the friction composites, it is clear that the determination of their chemical composition

Hutnické listy č. 5/2017, roč. LXX
ISSN 0018-8069

presents a very difficult analytical problem. Most of the analytical methods require decomposition of solid samples and their transfer to the solution [8, 9].

The diverse composition of brake composites containing some very poorly soluble components causes the decomposition of the materials to be very difficult and not achievable in one step. Multielementary direct analysis of solid samples is allowed by the X-ray fluorescence spectrometry (XRF). Preparation of the samples for analysis is very simple; brake linings can be analyzed directly by X-ray irradiation of the sample surface. The problem, in absence of suitable reference materials (RM), is the calibration of the spectrometer for this purpose. A prerequisite for using this method is the preparation of own RM of similar composition as commercial brake linings. [10, 11]

1. Experimental

1.1 Apparatus

An energy dispersive XRF spectrometer SPECTRO XEPOS (SPECTRO A. I., Kleve, Germany) was used for elemental analysis. For samples excitation, 50 W Pd end-window tube operating at max. 50 kV was used. The target changer, with up to 8 polarization and secondary targets, offers many various excitation conditions ensuring optimum determination of all elements from Na to U. For brake linings analysis Mo and Co secondary targets and Al_2O_3 and HOPG (highly oriented pyrolytic graphite) polarization targets were used. Measurements were performed in He atmosphere. Silicon drift detector with Peltier cooling achieves a spectral resolution of less than 160 eV for Mn K-α, the maximum count rate is 120 kcps. Special SPECTRO TurboQuant method for pellets was used for the preparation of the brake lining analysis method.

1.2 Preparation of reference materials

1.2.1 Components used for preparation of RM

The components used in brake linings production have been used for preparation of RM. When analytical grade materials or other materials with satisfactory declared purity were available, they were used for that purpose. The materials in question were Al_2O_3, $BaSO_4$, $CaCO_3$, SiO_2, ZnO, S, and powdered metals (Fe, Cu, Zn, Sn and brass). Furthermore, graphite, coke, zircon ($ZrSiO_4$), stibnite (Sb_2S_3), vermiculite, synthetic fibers Twaron, and phenol-formaldehyde resin were used. These materials were analyzed by EDXRF (SPECTRO XEPOS) and by AAS (UNICAM 969, UNICAM 989QZ) and/or ICP (SPECTRO CIROS VISION) methods after samples etching. The results of the analyses were used for the calculation of the chemical composition of the prepared RM. The grain size of most components was less than 50 µm, only the size of zircon grains was approx. 100 µm, and Twaron fibers had a diameter of 3 - 6 µm and length of 50 – 200 µm

1.2.2 Preparation of RM

The method developed for preparation of laboratory samples of friction composites was used for the preparation of RM. The components were weighed on analytical scales, mixed in a beaker and then milled and homogenized using a planetary micro mill FRITSCH pulverisette 7 and knife mill (blender) IKA M 20. Prepared mixture was transferred into the pressing vessel with a diameter of 32 mm. This operation should be performed with regard to the possible segregation of individual components, depending on their density and size and shapes of individual particles. The prepared mixture was pressed in a hydraulic press by force of 10 tons. The pellets were heat treated at 200 °C for 60 minutes. Seven pairs of RM of different composition were prepared. The composition of individual samples of reference materials is shown in Tab. 1.

Tab. 1 Elements concentrations in the prepared RM (wt. %)
Tab. 1 Koncentrace prvků v připravených RM (hm. %)

Element	FM 01	FM 02	FM 03	FM 04	FM 05	FM 06	FM 07
Mg	2.72	3.61	1.94	2.63	2.75	2.71	5.33
Al	1.09	1.40	0.818	0.57	6.97	6.87	4.29
Si	6.55	7.66	5.66	4.66	15.1	11.5	13.0
S	3.36	11.00	9.56	2.02	1.66	1.63	2.56
K	0.456	0.605	0.324	0.33	0.457	0.45	0.892
Ca	0.366	0.475	0.270	1.79	0.360	1.68	2.88
Ti	0.127	0.150	0.108	0.12	0.104	0.102	0.192
Fe	17.6	13.4	22.2	15.20	12.3	12.1	6.35
Cu	4.12	5.53	2.89	4.08	11.1	10.9	14.2
Zn	2.38	3.19	1.66	11.90	3.31	0.002	0.003
Sr	0.005	0.01	0.005	0.01	0.003	0.003	0.006
Zr	5.35	3.85	6.94	9.01	0.001	0.001	0.001
Sn	0.065	0.086	0.046	3.14	0.001	0.001	0.001
Sb	1.57	2.12	2.52	3.67	3.97	3.92	6.28
Ba	11.3	8.16	4.53	0.01	0.005	0.005	0.009

1.2.3 Assessment of the reference materials homogeneity

Homogeneity is a very important quality parameter of the RM for XRF calibration. Uniform distribution of each component is important to both the surface and the whole volume of material. To assess the homogeneity in the RM materials volume, the top and bottom of the pellets have been analyzed by XRF. Homogeneity of RM in their volume was calculated according to:

$$H = 100. (I_t - I_b) / \mathrm{I}\ (\%), \quad (1)$$

where I_t is the X-ray intensity of the monitored elements on the top and I_b on the bottom of pellets and I is their average concentration (top and bottom of the pellets). The top and bottom mean their orientation during pressing.

To assess the individual components distribution on the surface of pellets, every pellet was analyzed 7 times in the same position and 7 times in different places of the sample (6 places in the periphery and in the centre of pellet). Relative standard deviations (RSD) of the monitored elements intensity from the two measurements were compared. Distribution of individual components of the prepared RM was also examined using scanning electron microscope (SEM) Philips XL-30 equipped with X-ray spectrometer (EDAX).

2. Results and Discussion

An example of RM FM01 surface analysis using the SEM method is shown in Figure 1, where the phases identified in the marked positions are presented. Small particles of some components in the samples form clusters (barite, graphite, vermiculite, Fe), individual particles are visible at higher magnification. The surface structure of prepared samples corresponds with the commercial brake lining samples.

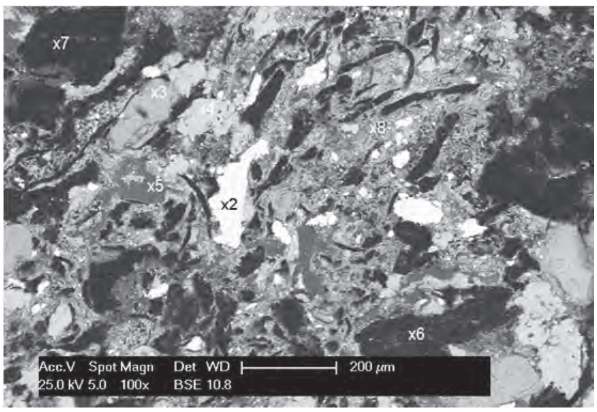

Fig. 1 SEM, backscattered electrons, 100× magnification, RM FM 01. Identified phases: 2 – barite, 3 – zircon, 4 – iron, 5 – vermiculite, 6, 7 – graphite, 8 - stibnite

Obr. 1 SEM, zpětně odražené elektrony, zvětšení 100×, RM FM 01. Identifikované fáze: 2 – baryt, 3 – zirkon, 4 – železo, 5 – vermikulit, 6,7, - grafit, 8 – antimonit

When the mixture is transferred into the pressing container, some components may segregate depending on their density, size, and shapes. This phenomenon can cause different concentrations of some elements on the top and the bottom of the pellets. The prepared pellets were, therefore, ground from both sides approximately by 0.1 mm in one step. Determinations of the monitored elements from both sides using the XRF method were performed after each grinding. In Fig. 2, evaluation of the monitored elements homogeneity is depicted according to the equation (1) in original samples and after three grinding steps. The figure shows that the bottom sides of the pellets are enriched by heavier components (Fe, Cu, Sn, and Zr), light components (vermiculite, ZnO) enrich the top sides of the pellets. After the third grinding step - approx. 0.3 mm removed -, the differences of the monitored elements concentrations in both sides of the pellets are not greater than 5%. Due to the nature of the prepared samples, it can be stated that the homogeneity of the distribution of individual components in the RM is satisfactory and it fulfills the given purpose.

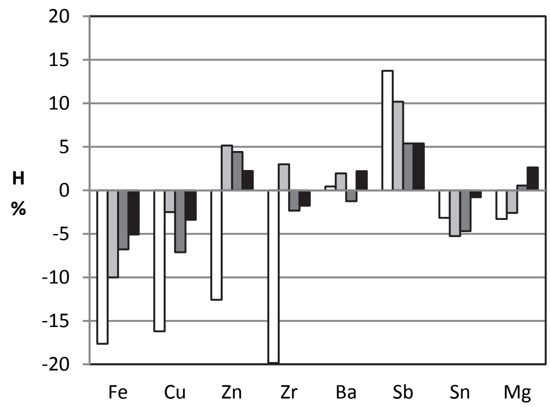

Fig. 2 Assessment of friction materials homogeneity in the pellets volume (H) for chosen elements after every abrasion; □ original material, ▩ after the 1st abrasion, ▩ after the 2nd abrasion, ■ after the 3rd abrasion

Obr. 2 Posouzení homogenity v objemu pelet (H) pro zvolené prvky po jednotlivých obroušeních; □ původní materiál, ▩ po prvním obroušení, ▩ po druhém obroušení, ■ po třetím obroušení

An example of surface homogeneity assessment of RM FM01 by XRF method is shown in Figure 3. RSD of the chosen elements for the X-ray intensities of 7 analyses in different positions and 7 analyses in the same position are compared. RSD calculated for the same position is in the range of 0.5 – 3%, only RSD of magnesium concentrations is slightly higher. RSD values of the analyses results in different positions include both the measurement uncertainty and the inhomogeneity of individual components distribution on the sample surface. These values lied in the range of 1 – 10 % but did not exceed 3% for most elements and they were approximately twice higher than the RSD for the analysis of the same elements in one position.

Hutnické listy č. 5/2017, roč. LXX
ISSN 0018-8069

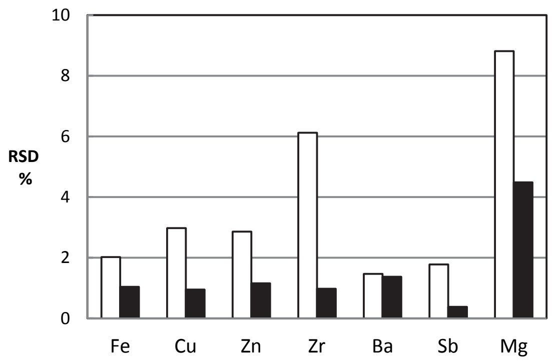

Fig. 3 Assessment of pellets surface homogeneity for chosen elements. Comparison of relative standard deviations of results of seven analyses in different positions and seven analyses in one position. □ different positions, ■ one position

Obr. 3 Posouzení homogenity na ploše pelet pro zvolené prvky. Porovnání relativní standardní odchylky výsledků sedmi analýz v různých polohách a sedmi analýz v jedné poloze. □ různé polohy, ■ jedna poloha

The measured values of intensities and calculated values of monitored elements concentrations in the RM were used to create calibration models using SPECTRO software. The accuracy of the results determined using the new calibration was verified by the analysis of the prepared RM and by comparing the results with the calculated values. An example of the evaluation of the results is shown in Figure 4. Differences between the measured and calculated values for most elements did not exceed 10%. Only Si - especially in the samples with higher content of vermiculite - and Fe showed greater differences. Taking into account the great diversity of composition of friction composites, we can consider the results to be satisfactory.

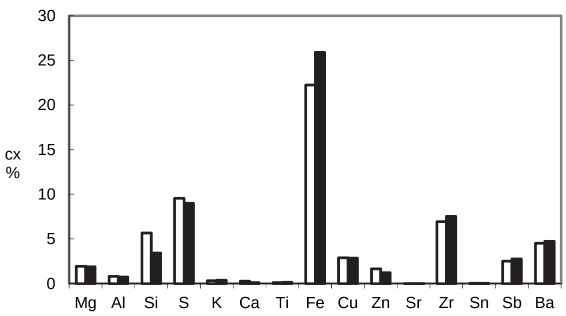

Fig. 4 Comparison of calculated and measured concentrations of some elements c_x in wt. % in the sample RM FM 03, □ calculated value, ■ measured value

Obr. 4 Porovnání vypočtených a naměřených koncentrací zvolených prvků c_x v hm.% ve vzorku RM FM 03, □ vypočtená hodnota, ■ naměřená hodnota

Conclusions

Friction composites used in automotive brake systems represent difficult analytical problem due to their very diverse composition. At our workplace, the method of direct chemical analysis of the friction composites used in automotive brake systems using X-ray fluorescence spectrometry (XRF) was developed. Seven reference materials (RM) of friction composites with different composition simulating wide scale composition of commercial brake linings were prepared. Homogeneity of material, which represents the greatest limitation of direct XRF analysis, was tested by the analyses of X-ray intensities of chosen elements by XRF. Volume homogeneity was tested by analyzing the top and the bottom of the prepared pellets. The differences for many elements were quite high and therefore both sides of the prepared pellets were ground down. The results were satisfactory after three steps of grinding (each of 0.1 mm) when the intensities of the monitored elements from both sides did not differ by more than 5%. Uniform distribution of components on the surface was tested by samples analysis in seven different places on the surface and seven times in one position. Although the RSD for the analysis in seven positions were approx. twice higher than that for analysis in one position, the results were satisfactory – for most elements they did not exceed 3%. Homogeneity of the prepared RM was found to be sufficient and, thus, they were used for calibration of X-ray fluorescence spectrometer. The accuracy of the calibration model was verified by the analysis of the prepared RM of known concentration using the new method. Differences between the measured and calculated values for most elements did not exceed 10%. These results are well within analytical expectations for this type of matrix and developed method is, therefore, suitable for the given purpose.

Acknowledgements

This paper was created within the project No. CZ.1.05/2.1.00/01.0040 "Regional Materials Science and Technology Centre" within the frame of the operational programme "Research and Development for Innovations" financed by the Structural Funds and from the state budget of the Czech Republic.

References

[1] FRIEDRICH, K. *Friction and Wear of Polymer Composites.* Amsterdam: Elsevier, 1986.
[2] BIJWE, J. *Polymer Composites*. 18 (1997) 378.
[3] SMALES, H. *Proc. Instn. Mech. Engrs.*. 209 (1995) 151.
[4] KNAPP, A., PILOATO, L. A. *Phenolic Resins, Chemistry. Applications and Performance.* Berlin: Springer – Verlag, 1987.
[5] P. FILIP, P., KOVAŘÍK, L., WRIGHT, M. A. *Automotive Brake Lining Characterization.* Society of Automotive Engineers, 1997.
[6] BREUER, B., KARLHEINZ, H. B. *Brake Technology Handbook*, SAE International Pennsylvania, USA, 2008.
[7] DANTE, R. C. *Handbook of Friction Materials and their Applications*, 2016, pp.79–153.
[8] MOSLEH, M., BLAU, P. J., DUMITRESCU, D. Characteristic and Morphology of Wwear Particles from Laboratory Testing of Disk Brake Materials. *Wear*, 256 (2004) 11-12.
[9] J. H. J. HULSKOTTE, G. D. ROSKAM, H. A. C. DENIER van der GON, *Elemental composition of current automotive braking materials and derived air emission factors*, Atmospheric Environment, 2014, 99, p. 436–445.
[10] BERTIN, E. P. *Principles and Practice of X-Ray Spectrometric Analysis*, Plenum Press, New York-London, 1975.
[11] TERTIAN, R., CLAISSE, F. *Principles of Quantitative X-Ray Fluorescence Analysis*, Hayden & son Ltd, London, 1982.

RELATED RESEARCH TOPICS

Research and development

- Development and optimisation of new technologies of highly pure materials, special metallic alloys and intermetallic compounds with defined structures and physical properties for applications in electronics, medicine, mechanical engineering and chemical industry.
- Development and optimisation of processes of powder technologies for production of selected types of materials and products.
- Control of specific properties of intensively rolled and thermo-mechanically processed materials using their structural potential.
- New sources of strength and toughness of materials for demanding technological applications.
- Research of metallic materials with ultrafine-grained structure (nanostructure), and development of processes for their preparation.
- Experimental verification of new technological procedures for metallic materials with high quality parameters.

ORGANISATION

1. Department of material preparation:
- laboratory of pure metals
- laboratory of preparation technology of special materials

2. Department of powder technologies:
- laboratory of magnetic and ceramic materials
- laboratory of friction composites

3. Department of forming processes:
- laboratory of severe plastic forming processes of materials
- laboratory of modelling and optimisation of forming technologies

4. Department of evaluation of material properties:
- laboratory of structural analysis
- laboratory of mechanical properties
- laboratory of chemical analyses
- laboratory of surface analyses and corrosion
- laboratory of physical properties of materials and nano-structures

5. Department of experimental verification of technologies and applications
- laboratory of experimental verification of technologies for manufacture of new materials
- laboratory of modelling of processes in liquid and solid phases

RESULTS

Between 2010-14: 5 patents, 50 applied research results and 250 impact articles.

www.rmtvc.cz/en

RMSTC
Regional Materials Science and Technology Centre