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Adhesion of Various Geopolymers Coatings on Metal Substrates

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This article deals with adhesion of various alkali-activated metakaolin-based geopolymer coatings on structural steel 1.0038 (according to EN 10025-2). This steel alloy was chosen in order to analysis adhesion of prepared geopolymer coatings. Our samples were characterized by laser and SEM microscopy and grid test was performed. Microscopy was performed to get knowledge about visible characterization and overall quality of prepared coatings. Based on previous research SEM results correspond with properties changes in coatings and their classification of grid test. Grid test was performed and results was evaluated. These results show potential of our prepared GP and could be used as base for further research and possible application as anti corrosion coatings in construction or fire-resistant barriers. The aim of the research was to prepare alkali-activated metakaolin-based geopolymer on a structural steel substrate, to evaluate the visual quality of the coatings and to evaluate the results of the grid test.

Keywords: geopolymer, structural steel, microstructure, grid test, adhesion

1 Introduction

Geopolymers (GP) are inorganic polymeric substances that belong to the group of alkali-activated materials. GP are synthetic aluminosilicate materials lying between ceramic materials and hydrated binders such as cement. Geopolymers are usually produced at low temperatures below 100 °C and they consist of chains or networks of mineral molecules linked by covalent bonds [1-7].

GP are close to natural zeolites because their structures are similarly composed of Si-O-Al polymer networks. The main difference is the amorphous character of GP, while zeolites are crystalline [8-10].

The history of GP dates back to 1978, when they were first described by prof. Davidovits [11]. The term Geopolymer refers to a class of solid bodies that are formed by synthesizing aluminosilicate powder with an alkaline solution. GPs are characterized by high heat resistance and resistance to direct contact with fire [12].

The study of substrate properties is important for coatings suitability. For the substrate was used structural steel 1.0038 (according to EN 10025-2). The surface properties and the contact angle have a significant effect on the adhesion properties, which give GP corrosion resistance, heat resistance and reduced thermal expansion of the substrate [13].

We chose painting with brush to get geopolymer coatings on the metal substrates. The painting is the cheapest and user friendly method. It's possible to use different way such as spraying or dipping [13-16].

The aim of the research was to prepare alkali-activated metakaolin-based geopolymer on a structural steel substrate, to evaluate the visual quality of the coatings and to evaluate the results of the grid test [17,18].

2 Materials and methods

The geopolymer suspension is applied to the underlying substrate made of structural steel 1.0038 (according to EN 10025-2). Before applying the suspensions, the surface of the substrate has to be cleaned and degreased with an organic solvent (acetone) without further pretreatment of the surface.

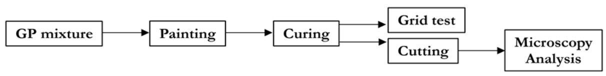


Fig. 1 *Scheme of preparation GP coatings and measurment of all samples*

The suspensions were applied with a regular brush designed for water-based paints. It is necessary to apply a very small amount of suspension and spread it perfectly over the surface, thus creating a very thin layer of geopolymer, which is essential for the final quality of the geopolymer coating.

In order for geopolymer suspensions to acquire their final properties after application to the underlying substrate, chemical reactions, so-called geopolymerization, must occur in the mixture [19,20]. For the geopolymer mixtures geopolymerization occurs at elevated temperatures, in contrast to mixtures with a different composition, where geopolymerization can occur at lower temperature [19,20]. For the selected geopolymer mixtures, it is necessary to reach a certain minimum temperature, which was experimentally determined to be 170 °C

[21]. This temperature is important parameter influencing the resulting quality of the coatings. This increasing of temperature is needed for the geopolymerization process.

2.1 Chemical composition of GP

From previous investigations of many types of GP mixtures, the following GP suspensions have been selected, which achieve very good surface quality results and are suitable for coating metallic materials. In the case of GP suspensions on metal base materials, analysis are mainly focused on researching the properties and improving the quality of the surface. The resulting composition of GP suspensions for metal underlying substrates is shown in the Tab. 1 below.

Tab. 1 *Marking and composition of GP suspensions for metal substrates*

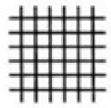
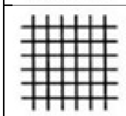
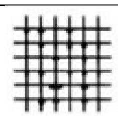
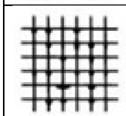
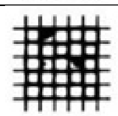
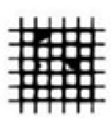
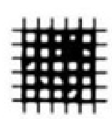
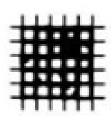
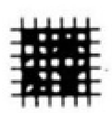
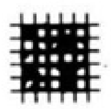
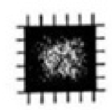
Designation GP suspension	Acronym for suspensions	Ingredients
G	H^+ matrix modified with aluminosilicate	H_3PO_4 with kaolin KDG in H_2O
H	H^+ matrix modified with aluminosilicate	H_3PO_4 with kaolin KDG in H_2O and iPrOH with fine graphite
I	H^+ matrix modified by Al	H_3PO_4 with $Al(OH)_3$ in iPrOH
J	H^+ matrix modified by Al	H_3PO_4 with nano Al_2O_3 in iPrOH
K	Al-modified acidic matrix	H_3PO_4 with nano Al_2O_3
L	H^+ matrix modified with aluminosilicate	H_3PO_4 with kaolin KDG in iPrOH
M	Al-modified SiBP matrix	Sodium water glass modified B+P with nano Al_2O_3
N	Al-modified SiP matrix	SiP matrix with nano Al_2O_3

The Tab. 1 contains an overview of basic GP suspensions that were analyzed on metal substrates and basic research was carried out. During subsequent testing, the types of GP mixtures will be reduced according to specific analyzes and their results.

2.2 Grid test

Adhesion of geopolymer suspensions to the substrate was analyzed by the grid test method according to ISO 2409 [22], specifically with the Elcometer 1542 grid test set. The knife used had a blade spacing of 1 mm for coatings with a thickness of 0–60μm. Table 2 shows the parameters for evaluating the adhesion test according to the ISO 2409 standard.

Tab. 2 *Evaluating the grid test according to ISO 2409 [22]*

Example appearance		Description	Classification ISO 2409
Minimum removal	**Maximum removal**		
		The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	0
		Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5% is affected.	1
		The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5%, but not greater than 15%, is affected.	2
		The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15%, but not greater than 35%, is affected.	3
		The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partially or wholly. A cross-cut area greater than 35%, but not greater than 65%, is affected.	4
		Any degree of flaking that cannot even be classified by classification 4.	5

First, a cut is made by using a six-row knife. Subsequently, a second cut is made, perpendicular to the first cut. The blade of the knife must pass through the coating of the geopolymer suspension and hit the surface layer of the substrate. A grid will be created, which can be cleaned of dirt and, if necessary, of the peeled coating with the help of a brush. The next step is to stick the adhesive tape on the created grid and then tear it off at an angle of 60 °. This will break off non-cohesive parts of the coating that could not be removed during cleaning with a brush. After the cleaning process, the grid is rated from category 0 to 5 according to the criterion of how much coating has peeled off around the cuts.

3 Results

3.1 Scanning electron microscopy and Laser microscopy

A Tescan Vega 3 scanning electron microscope (SEM) and LEXT OLS 5000 SAF 3D laser confocal microscope (CLSM) were used for microstruture and 3D images of various geopolymers. All samples had microsturture and detail images supplemented with 3D scans of GP which shows surface characteristic of the each GP coatings. These characteristic were describe below each GP sample. For LEXT images was used 200x magnification with color and height images.

All prepared samples were cut into small pieces with no extra preparation for SEM measurement. This is need for measuring in SEM chamber. After that are real prepared surfaces shown.

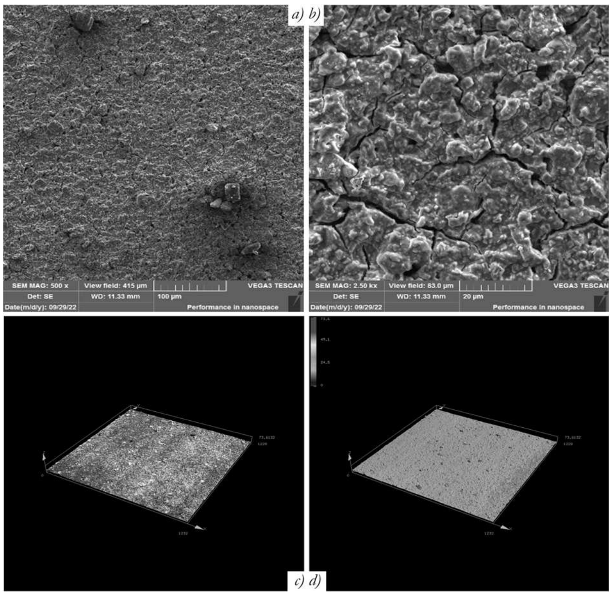


Fig. 2 *Microstructure of geopolymer G;*
a) low magnification b) detail c) color d) height

It can be seen from the images that the resulting surface of geopolymer G is broken, but the distribution is uniform. In electron microscopy images, it is also possible to observe larger particles, probably coming from the surface of the substrate. At a higher magnification, cracks in the substrate can be observed, which are again evenly distributed over the entire surface. However these cracks do not affect the integrity of the surface or its adhesion. Height image shows large agglomeration on the top of the coating.

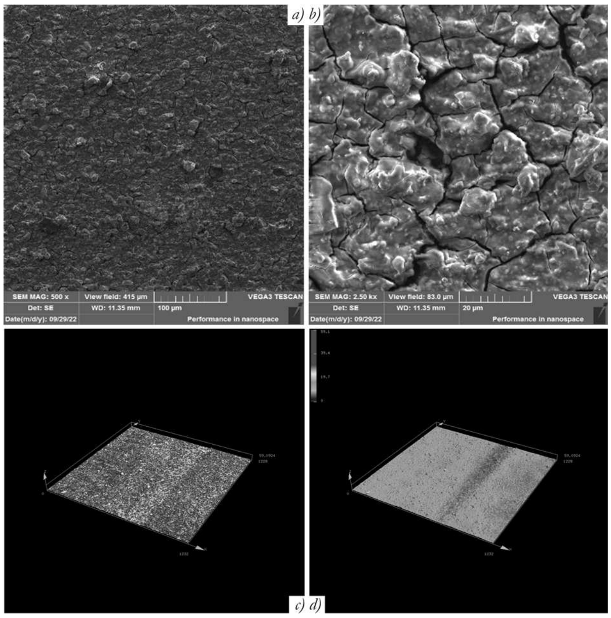


Fig. 3 *Microstructure of geopolymer H;*
a) low magnification b) detail c) color d) height

Geopolymer H, like G, shows a rough surface structure with a uniform distribution. At a higher magnification, cracks in the substrate can again be observed, which reach a larger size and frequency, again without affecting the integrity of the surface and adhesion to the underlying substrate. Height image shows agglomeration on the top of coating.

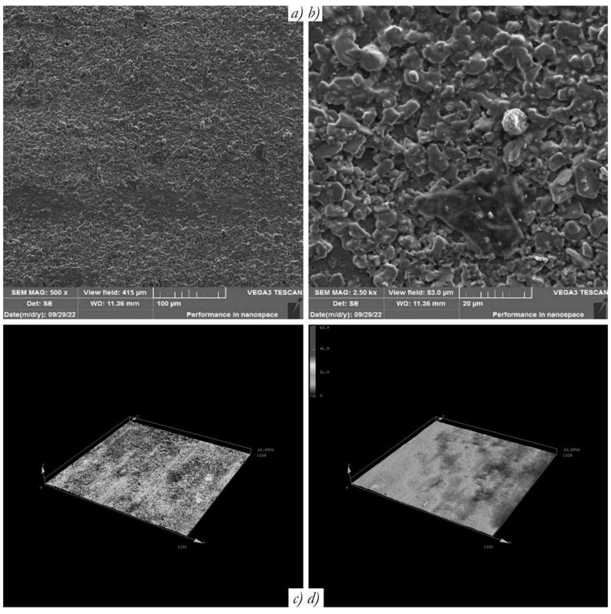


Fig. 4 *Microstructure of geopolymer I;*
a) low magnification b) detail c) color d) height

Geopolymer I already shows a smoother surface structure. There are visible agglomeration with uniform distribution in the coating without affecting the integrity. Height image shows uneven surface with couple agglomeration spots on the top of the coating.

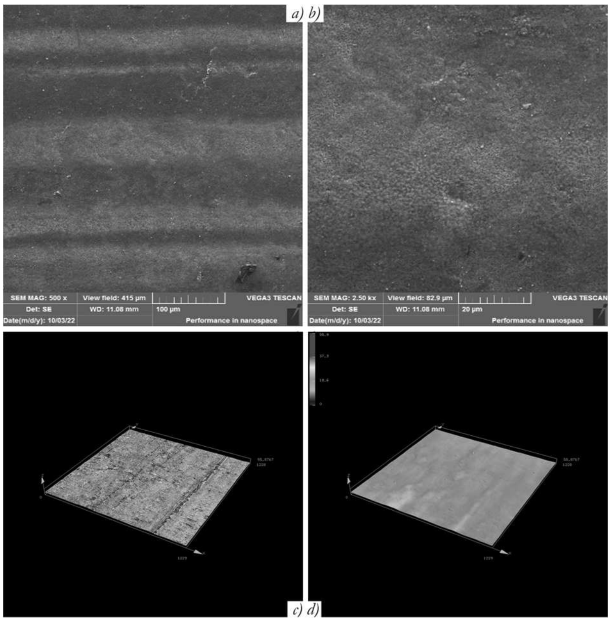


Fig. 5 *Microstructure of geopolymer J;*
a) low magnification b) detail c) color d) height

With geopolymer J, a very fine surface structure and a very even distribution of the coating without defects can be observed. Surface integrity is very good with no visible cracks. Height image shows fine flat surface with no visible agglomeration.

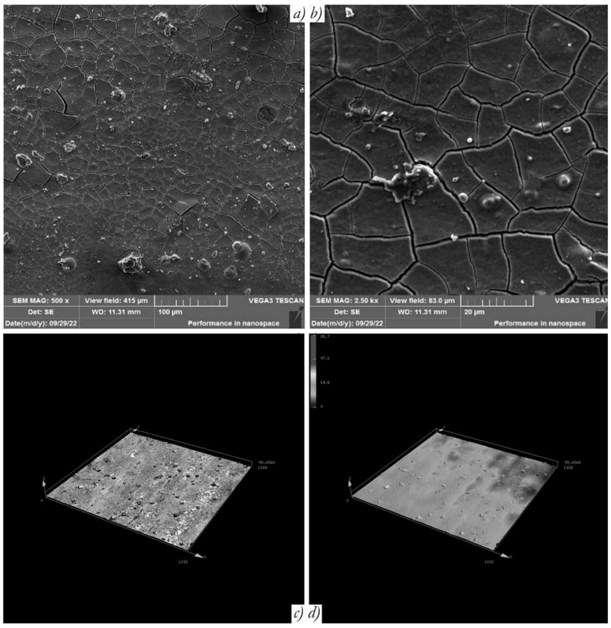


Fig. 6 *Microstructure of geopolymer K;*
a) low magnification b) detail c) color d) height

For geopolymer K, slight defects in the coating can be observed. Larger particles can be seen. Cracks in the coating are clearly visible, especially in the parts where a thicker layer of geopolymer is apparently applied. But even here, the cracks are evenly distributed, with the same size. Also this not affect the adhesion of the coating to the surface. Height image shows agglomeration on top of the coating.

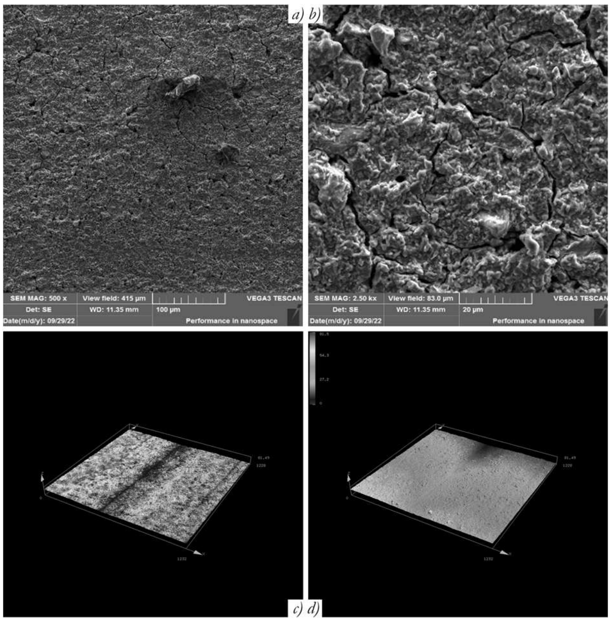


Fig. 7 *Microstructure of geopolymer L;*
a) low magnification b) detail c) color d) height

Geopolymer L shows a coarse surface structure with uniform distribution. At a higher magnification, cracks can be observed that are not very evenly distributed, but even here they do not affect the adhesion of the coating to the underlying substrate. Height image shows relative flat surface with agglomeration. Color image shows brushing mark in the middle.

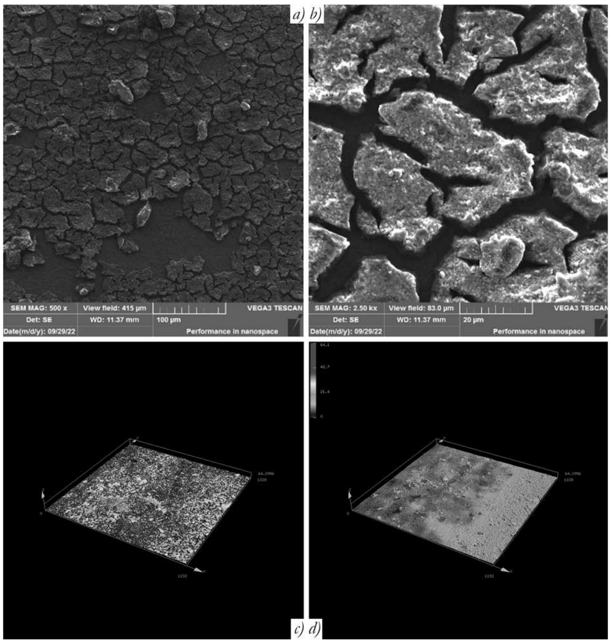


Fig. 8 *Microstructure of geopolymer M;*
a) low magnification b) detail c) color d) height

Geopolymer M shows larger defects in the coating. It is possible to see a high degree of fragmentation of the surface, and above all, large, wide cracks that cause large areas of the coating to peel off to the underlying substrate. Height image shows uneven surface with spot and right side area agglomeration.

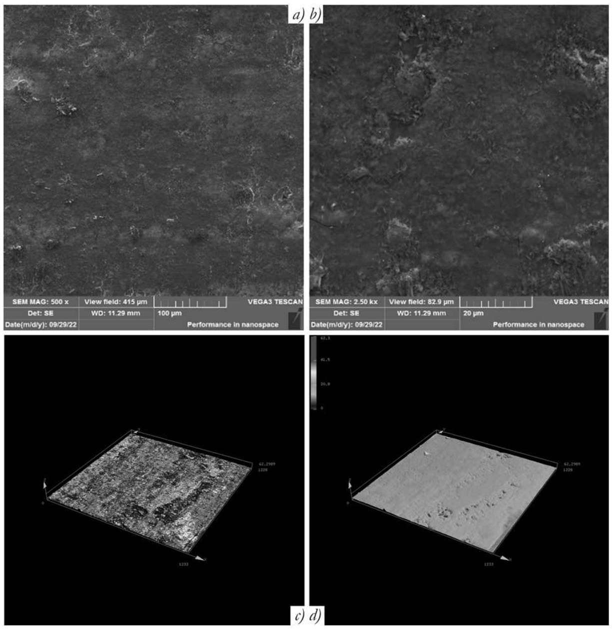


Fig. 9 *Microstructure of geopolymer N;*
a) low magnification b) detail c) color d) height

Geopolymer N shows uneven surface structure, with little fragmentation. No cracks are visible. Height image shows couple holes in the relatively flat coating with no agglomeration.

Crack measurement results show very different values where geopolymers I, J and N do not have visible or measurable cracks. The remaining geopolymers have measurable cracks. Geopolymer K had the smallest value with a value of 0.088 μm. Other geopolymers G, H and L had values around 250 μm. Geopolymer M had the highest value of 0.511 μm and at the same time had the best value in the grid test.

Tab. 3 *Comparation of cracks in each GP coatings on Fe substrate*

Sample	Average size of cracks [μm]
G	0.256
H	0.272
I	Ø
J	Ø
K	0.088
L	0.210
M	0.511
N	Ø

3.2 Grid test of GP on contruction steel

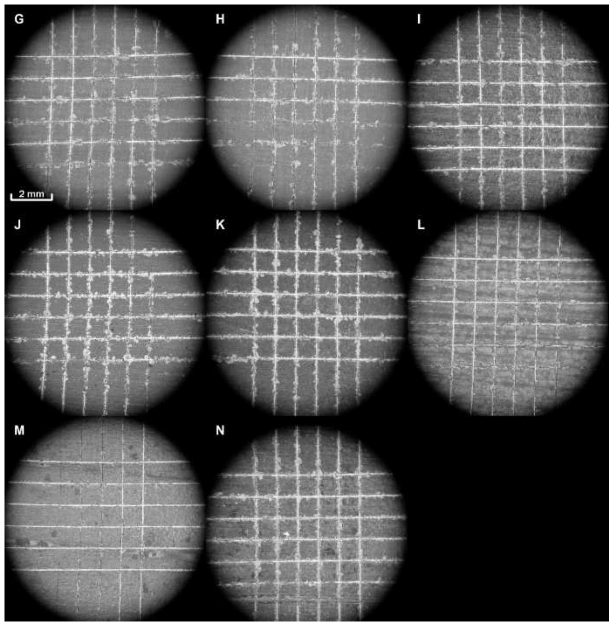


Fig. 10 *Grid test of G-N geopolymers on the Fe substrate (15x magnification)*

Tab. 4 *Evaluation of grid test of G-N geopolymers on Fe underlying substrate*

Substrate	Designation of geopolymer suspension							
Fe	G	H	I	J	K	L	M	N
Rating	2	2	2	3	3	2	1	2

Table 4 show evaluated results of grid test of various GP on Fe substrate. Suspensions J and K achieved a value of 3 in the assessment of adhesion to the substrate, i.e. separation of 15-35 % of the coating area from the substrate. Suspensions G, H, I, L and N achieved a rating of 2, i.e. separation of 5-15 % of the coating area from the substrate, and suspension M achieved the highest rating of 1, i.e. separation of the coating area not exceeding 5 %. Overall (except suspension M), the suspensions applied to the underlying Fe substrate do not achieve as high adhesion as the suspensions on the Al substrate from previous research [20].

4 Conclusion

The basis of this work was the application of GP coatings using a brush on construction steel alloy underlying substrates in order to determine the quality of the applied layers using a cheap and inexpensive technique. All geopolymers suspensions with different chemical compositions were characterized and compared.

Geopolymers J and N shows smoothest surfaces of all GP. Geopolymers G, H, I and L shows rough surfaces with visible cracks in coatings. Geopolymers K and M shows defects in structure of these coatings with very rough surfaces.

In the grid test of the adhesion of the layer to the construction steel underlying substrate, geopolymer M achieved a rating of 1, i.e. separation of the coating along the section with a total area of up to 5 %, geopolymers G, H, I, L and N rated 2, where the area of the separated coating is 5-15 %. Geopolymers J and K were the worst, with a rating of 3, i.e. separation of 15-35 %.

The evaluation of the grid test shows that the adhesion of the selected geopolymer suspensions is for construction steel underlying substrate do not achieve high adhesion (except geopolymer M).

Of the obtained results, Geopolymer M turned out to be the best, which achieved the best value in the grid test and is therefore a suitable candidate for further research.

In the 3D scanner, a large amount of agglomeration was observed on the surface of the coatings for geopolymers (G, H, L and M) and a smaller amount of agglomeration for geopolymers (I and K). Only geopolymers J and N had no visible surface agglomeration.

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