Marko Pavlović[1], Marina Dojčinović[2], Muhamed Harbinja[3], Atif Hođić[3], Mirjana Stojanović[4], Zoran Čeganjac[5], Zagorka Aćimović[4]*

NEW TYPES OF PROTECTIVE COATINGS AND DEVELOPMENT OF TEST METHODS

NOVE VRSTE ZAŠTITNIH PREMAZA I RAZVOJ METODA ISPITIVANJA

Originalni naučni rad / Original scientific paper
UDK /UDC:

Rad primljen / Paper received: 5.10.2023

Adresa autora / Author's address:
[1)] University of Belgrade, Innovation Centre of the Faculty of Mechanical Engineering, Belgrade, Serbia
[*]email: pavlovic.marko38@gmail.com
[2)] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
[3)] Innovation Scientific Development Centre (INRC), AD Harbi Ltd., Sarajevo, Bosnia and Herzegovina
[4)] Engineering Academy of Serbia
[5)] Academy of Vocational Studies Šumadija, Aranđelovac Department, Serbia

Keywords
- mullite
- cordierite
- zirconium silicate
- pyrophyllite
- protective coating
- cavitation resistance

Ključne reči
- mulit
- kordijerit
- cirkonijum silikat
- pirofilit
- zaštitni premazi
- kavitaciona otpornost

Abstract

The paper presents the results of synthesis and characterisation of refractory coatings based on various fillers intended for the protection of metallic structures. Refractory fillers applied are based on mullite, cordierite, zirconium silicate, and pyrophyllite. Refractory filler samples are treated by micronization grinding down to 15 μm filler particles. Methods as XRD, SEM, and optical microscopy are used for characterisation. Performed tests determined the optimal composition of protective coatings and manufacturing processes. According to standard ASTM G32 an ultrasonic vibrational method with stationary sample was used for characterising the obtained coatings. The goal of the research was to determine the coating quality and its applications in metallic surface protection in conditions of wear, corrosion, cavitation, and high temperature. All coatings were tested under the same conditions. A comparison of cavitation resistance is given for tested coatings. Coating quality is evaluated based on cavitation loss rate and on the analysis of sample surface damage formation and development under effects of cavitation.

Izvod

U radu su prikazani rezultati sinteze i karakterizacije vatrostalnih premaza na bazi različitih punioca namenjenih za zaštitu metalnih konstrukcija. Korišćeni su vatrostalni punioci na bazi mulita, kordijerita, cirkonijum silikata i pirofilita. Uzorci vatrostalnih punioca podvrgnuti su mikronizirajućem mlevenju na veličinu zrna punioca 15 μm. Za karakterizaciju dobijenih punioca korišćene su metode XRD, SEM i optička mikroskopija. Ispitivanjem je određen optimalni sastav zaštitnih premaza i postupci njihove izrade. Za karakterizaciju dobijenih premaza primenjena je ultrazvučna vibraciona metoda sa stacionarnim uzorkom prema standardu ASTM G32. Cilj ispitivanja bio je određivanje kvaliteta premaza i mogućnosti primene za zaštitu metalnih površina u uslovima habanja, korozije, kavitacije i povišenih temperatura. Svi premazi su ispitivani pod istim uslovima. Prikazan je uporedni pregled kavitacione otpornosti ispitivanih premaza. Kvalitet premaza ocenjen je na osnovu vrednosti kavitacione brzine, analize nastajanja i razvoja oštećenja površine uzoraka pod dejstvom kavitacije.

INTRODUCTION

Coatings with a good combination of wear resistance, high hardness and strength properties are used to protect parts of metallic structures exposed to rigorous operating conditions, /1-3/. To increase the resistance of hydraulic components to effects of cavitation, the application of various coatings and linings is justified, considering that failure under effects of cavitation is a surface degradation mechanism. A large amount of research is devoted to the use of non-metallic materials (ceramics and polymers) under cavitation conditions, /4/. Protective coatings can also be based on different refractory fillers (TiN; TiO_2; NiN; NiTi; NbN; WC; VC; WC-10Co-4Cr), with organic binders and solvents and are often used for equipment exposed to cavitation /5/. The manufacture of these coatings is carried out by modern process synthesis (CVD process, plasma spraying process, application of lasers, sol-gel processes, etc..) and in this way, it increases the resistance property to cavitation damage of metallic surfaces, /6/.

In our earlier research /7-10/ refractory materials mullite, cordierite, zirconium silicate, and pyrophyllite were used as fillers for protective coatings with an organic binder based on epoxy resin, organic additives, and a solvent that showed satisfactory resistance to the effects of cavitation. The paper presents the test results of new compositions of these protective coatings with modified procedures for the preparation of refractory fillers. The organic binder content was increased, and by additional micronization grinding of all tested refractory fillers, filler grain sizes of 15 μm were obtained. The goal was to obtain a coating with increased resistance to effects of cavitation, the possibility of comparative tests and quality evaluation of individual coatings for practical applications for protecting metallic surfaces.

EXPERIMENT

Four types of refractory materials were used as fillers in the composition of coatings for the protection of metallic structures: mullite (M), cordierite (C), zirconium silicate (ZS), and pyrophyllite (P). These materials were selected due to their properties, as well as the existence of a potential raw material base for their synthesis. For all research on synthesis of protective coatings, the samples of refractory materials were ground to a filler grain size of 15 μm.

Mullite (chemical formula $Al_6Si_2O_{13}$) is characterised by good stability of volume and strength at high temperatures, high resistance to creep and thermal shock, low thermal expansion and conductivity, corrosion resistance to slag, alkalis, liquid metals, corrosive gases, high resistance to abrasion and erosion, resistance to effects of cavitation. All this makes it an attractive material for the production of both traditional and advanced ceramics. A mixture of kaolin and alumina with the addition of a mineralizer (1 % NaF) was used for the synthesis of mullite. Alumina is added to the mix to achieve a 3:2 stoichiometric ratio of mullite. The mixture is homogenized, moistened with water and pressed. The synthesis of mullite took place in a Netzsch high-temperature laboratory furnace at 1450 °C with a heating rate of 10 °/min in an air atmosphere, /7/.

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) is characterised by the following properties: high refractoriness, high hardness, high density, low value of dielectric constant, low coefficient of thermal conductivity, low coefficient of linear thermal expansion, high resistance to thermal shock, relatively high melting temperature with the possibility of application up to 1380 °C, high inertness to liquid metal. It is an important refractory material for research and wide application in the fields of: electrothermia, electronics, for the manufacture of special structural parts in mechanical engineering, the automotive industry, for the special needs in the chemical industry, the industry of refractory materials. Cordierite is obtained by a high-temperature reaction in the solid state, in which the standard raw materials talc, kaolin, and alumina are used for the synthesis. The starting mixture for the synthesis has the following composition: 36 wt.% talc, 29 wt.% kaolin, 35 wt.% alumina. The starting materials for the cordierite mass, except kaolin, are ground to a grain size of 0.1 mm and then mixed in the ratio $2MgO : 2Al_2O_3 : 5SiO_2$. After homogenization, the powder mixture is pressed on a 'Lais' type press under the pressure of 1 MPa, and then samples are sintered at 1300 °C for 8 hours in a laboratory furnace in an oxidizing atmosphere, /8/.

Zirconium silicate ($ZrSiO_4$) is an attractive refractory material widely used for the synthesis of new materials due to its properties: high melting temperature, or high refractoriness, low coefficient of thermal and linear expansion, high resistance to thermal shock. An important application of this refractory material is for the production of zirconium metal, zirconium compounds, in foundries for the manufacture of sand moulds and cores for casting high-quality steel castings, for the production of refractory coatings for moulds and cores, as well as the manufacture of ceramic shells in precision casting. Filler samples for research are obtained by mechanical processing, purification and grinding of high-purity zircon sand (99.99 wt.% $ZrSiO_4$) to a filler grain size of 15 μm, /9/.

Pyrophyllite ($Al_2Si_4O_{10}(OH)_4$) is a mineral raw material suitable for the production of a wider range of products and applications in various branches of the economy (construction, agriculture, paper industry). It has characteristic softness, crystalline structure, good grindability, low coefficient of thermal conductivity, low coefficient of linear thermal expansion. It has a great ability to stick and coat surfaces, a high melting point, high inertness, i.e., resistance to acids, alkalis, and heating. To investigate the possibility of using pyrophyllite as a filler in the composition of protective coatings, the initial sample of pyrophyllite rock from the Parsović-Konjic deposit (Bosnia and Herzegovina) was ground to grain size of 15 μm, /10/.

The composition of the tested coatings (wt.%): refractory filler (80-85); binder based on epoxy resin (15-17); organic additives (1-1.5); organic solvent to a coating density of ρ = 2.5 g/cm^3. During the synthesis of the coating, all components from the coating composition were gradually added with constant mixing. For testing, the obtained protective coatings were applied in two layers to a metal plate, and then dried in the air for 60 minutes.

Samples of refractory fillers were analysed using an X-ray diffractometer, Philips model PW-1710. The morphology of the damaged surfaces of the samples was analysed using a scanning electron microscope model Joel JSM 6610 LV.

To determine the resistance properties of the obtained protective coatings, the ultrasonic vibration method with a stationary sample was applied according to the ASTM G32 standard, /11/. The testing methodology is described in earlier works, /7-10/. The time of exposure of samples to the effect of cavitation (min) is: 15; 30; 45; 60. Coating mass loss was monitored as a function of cavitation time and the cavitation speed was determined. Based on cavitation speed value, analysis of surface damage morphology, the cavitation resistance of the tested protective coatings is determined. A comparative overview of cavitation resistance of the tested coatings is presented as a basis for choosing a coating for application in appropriate conditions of exploitation.

RESULTS AND DISCUSSION

Chemical composition of the initial samples of refractory fillers, based on mullite (M), cordierite (C), zirconium silicate (ZS), and pyrophyllite (P), was examined by standard analytical methods, and the obtained results are shown in Table 1. For the synthesis of the coating, the refractory fillers were micronized to a grain size of 15 μm. In relation to earlier research results, /7-10/, in order to improve resistance properties of protective coatings, the coating composition was changed: 80-85% refractory filler; 15-17% binder based on epoxy resin; with organic additives and organic solvent.

Figure 1 shows coating sample surfaces before and during the cavitation test.

A short incubation period lasting about 3 min was observed when there was no mass loss. After that, slight damage to the coating surface occurs, which develops at a low speed. After 30 min of exposure, shallow pits appear, which change slightly during further testing up to 60 min. The pits slightly change their shape and dimensions during the test under the effect of cavitation, which indicates an increased resistance of the coating surface to the effect of cavitation. Figure 2 shows the appearance of pits on the surface of the tested coating samples after 60 minutes of exposure. A comparative examination of the surface of the coating samples during the cavitation test shows that coatings based on mullite and cordierite have the least surface damage, which can also be seen in the sample mass loss diagram during the cavitation erosion test, Fig. 3.

Table 1. Chemical composition of refractory fillers.

Filler	Oxide content (%)						
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O+K_2O	ZrO_2
M	27.89	71.80	0.06	0.10	0.05	0.02	-
C	51.01	30.09	1.20	13.10	3.20	0.02	-
ZS	32.80	-	-	-	-	-	67.20
P	62.56	14.92	1.22	1.45	7.32	1.07	-

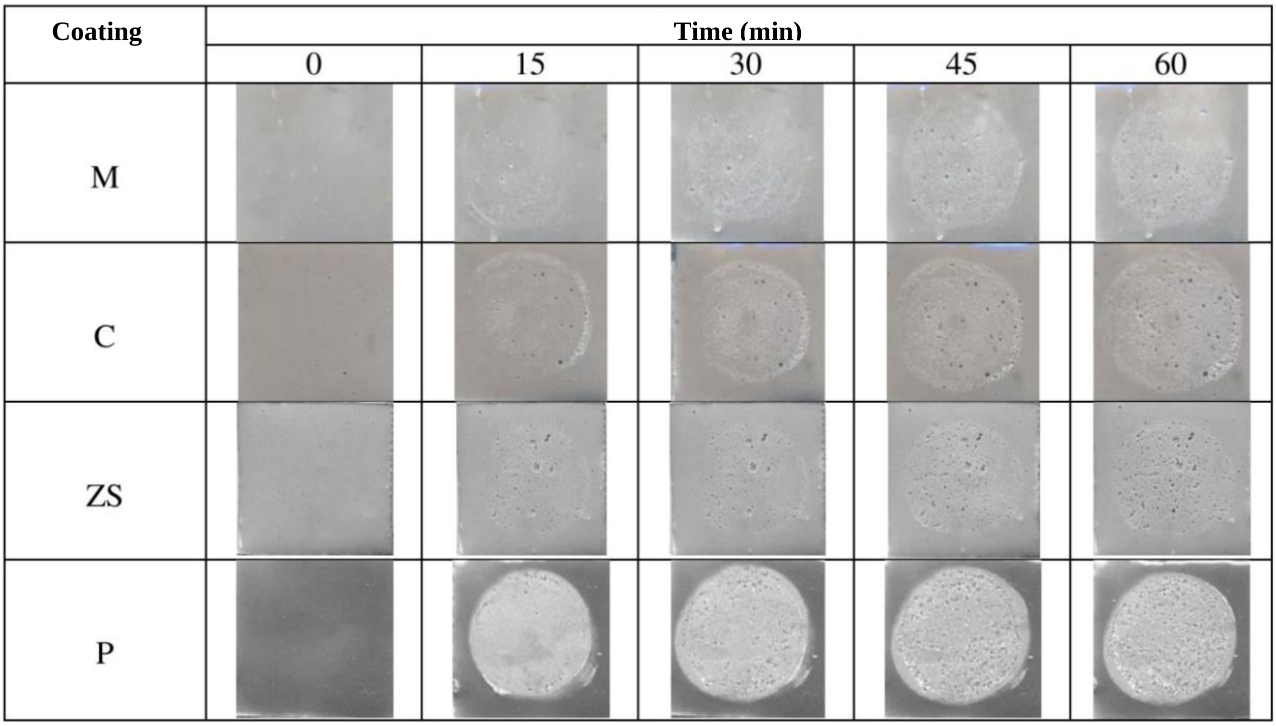

Figure 1. Photographs of coating sample surfaces before and during the cavitation test.

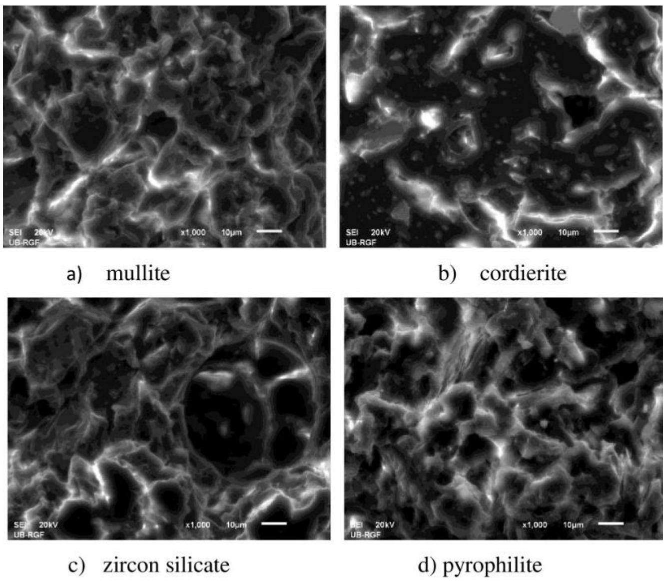

Figure 2. SEM microphotographs of surfaces of the tested coating samples after 60 minutes of exposure.

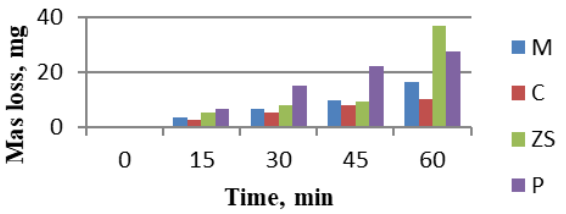

Figure 3. Protective coating mass loss from samples based on mullite (M), cordierite (C), zirconium silicate (ZS), and pyrophyllite (P) during the cavitation erosion test.

Coatings based on zirconium silicate have the greatest changes on the surfaces of samples. During the exposure, deeper pits appear and develop, which are connected on certain parts of the surface of the samples. In the case of samples based on pyrophyllite, shallow pits occur mostly around the perimeter of the sample, the development of damage is gradual.

Samples of cordierite (10.16 mg), followed by mullite (16.49 mg), pyrophyllite (27.69 mg) show the lowest mass loss during 60 min exposure, and the sample of zirconium silicate (36.97 mg) shows the highest mass loss. The resistance of tested coating samples under the effect of cavitation is evaluated based on calculated values of cavitation rates: cordierite V = 0.169 mg/min; mullite V = 0.275 mg/min; pyrophyllite V = 0.462 mg/min; zirconium silicate V = 0.616 mg/min.

The higher cavitation resistance of the examined protective coatings based on cordierite and mullite can be explained by the high properties of applied fillers, above all, high hardness and strength, stability at high temperatures and under pressure. Coatings based on pyrophyllite have lower hardness but have a great ability to stick and cover surfaces, a high melting point, high inertness, i.e., resistance to acids, alkalis, and heating, which makes it important for potential applications. Coatings based on zirconium silicate are used in foundry practice to protect sand moulds and cores. For further research, the possibility of applying mixtures of this filler with other refractory materials for the synthesis of protective coatings for metal structures is interesting.

CONCLUSION

Research has shown that protective coatings based on mullite, cordierite, zircon silicate, and pyrophyllite have satisfactory resistance to the effects of cavitation. This is new research considering that these types of refractory products have not been used in practice. Coating recipes and their synthesis procedures are defined through research. Methods for characterising refractory coatings using the ultrasonic vibration method with a stationary sample, scanning electron- and optical microscopy have been defined that enable rapid examination and assessing the possibility of applying the coating under given conditions of exploitation. Future research should focus on the application of refractory fillers based on a mixture of different types of powders with different granulometric composition which will enable the improvement of the mutual packing of the filler particles in coating layers, improvement of coating characteristics and reduction of costs. Also, the application of organic additives will improve the dispersion of the coating. To expand the range of coating applications, the possibility of adding various pigments to achieve the desired coating colour can be explored.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract no.451-03-47/2023-01/200135).

The authors are especially grateful to the Innovation Scientific Development Center (INRC), AD Harbi Ltd., at Sarajevo Bosnia and Herzegovina, for their cooperation and wholehearted assistance during the research of protective coatings based on pyrophyllite.

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